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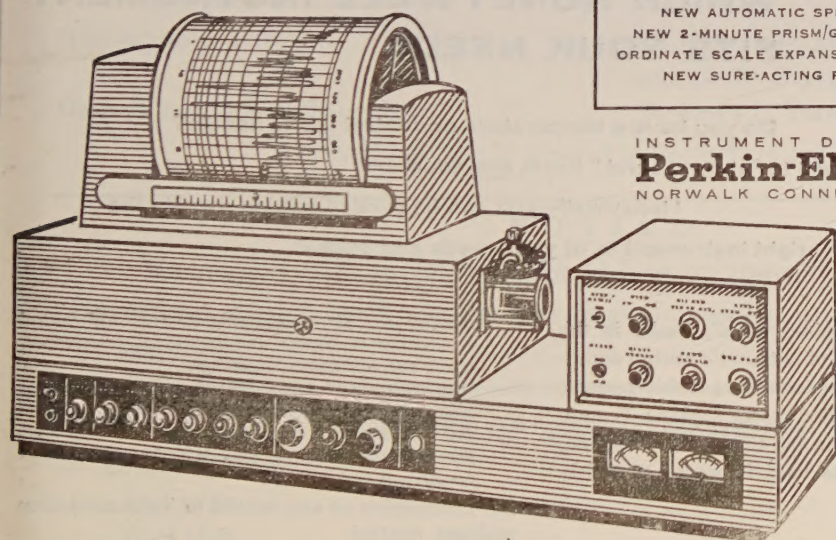
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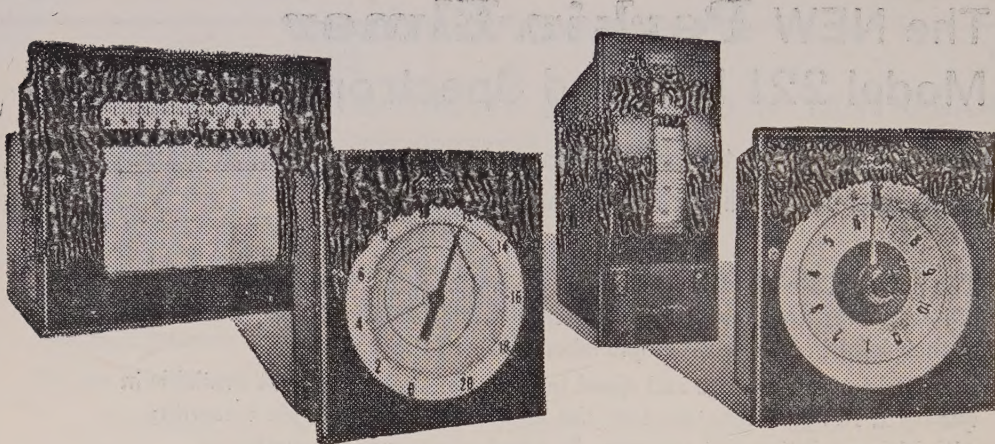
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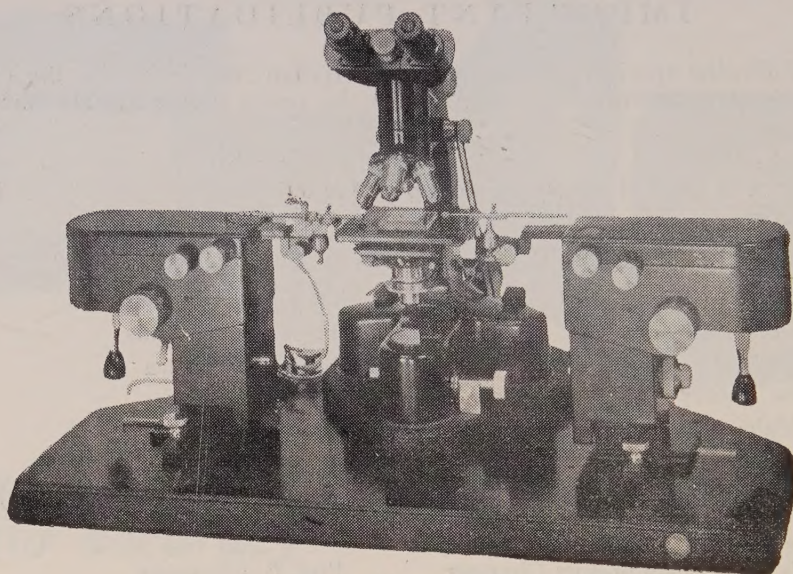
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INFLUENCE OF ENVIRONMENT ON THE RAMAN AND INFRARED SPECTRA OF QUINOLINE AND TETRALIN*

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(Received August 14, 1961)

Plate XI

ABSTRACT. The Raman spectra of quinoline and tetralin in the liquid state and in the solid state at -180°C and also the infrared spectra of the liquids and their solutions in some aliphatic solvents have been investigated and an attempt has been made to assign the prominent Raman and infrared frequencies of quinoline to some of the vibrational modes of the molecule.

In the solid state at -180°C quinoline exhibits a moderately strong new Raman line 49 cm^{-1} . On the other hand, tetralin at -180°C shows two new low-frequency Raman lines of shifts 61 and 92 cm^{-1} respectively under similar conditions. It is found that some of the lines due to intramolecular modes of vibration of both the compounds undergo changes with the solidification of the liquids. The results have been compared with those due to benzene and naphthalene and it has been suggested that the changes mentioned above and the appearance of the new low-frequency Raman lines may be due to intermolecular coupling in the crystal at the low temperature.

INTRODUCTION

It was observed by Sirkar and Ray (1960) that the crystals of benzene at -100°C show only three Raman lines in the low-frequency region and the number of these lines increases to five when the temperature is lowered to -180°C . In the case of pyridine at -180°C , however, only four such lines were observed by Kastha (1956). The increase in the number of low-frequency lines with lowering of temperature of the crystals was also observed in the Raman spectra of many substituted benzene compounds such as *p*-xylene (Biswas, 1954a), *p*-bromotoluene (Biswas, 1954b) and *m*-dichlorobenzene (Biswas, 1955). It has also been pointed out by Biswas (1957) that the number of the low-frequency lines does not depend on the shape and size of the molecule, but it depends on the nature of the substituents. In the case of naphthalene at -180°C six such lines have been observed (Ray, 1960). It would be interesting to compare the spectrum of naphthalene

*Communicated by Professor S. C. Sirkar.

with that of quinoline, because the shapes and sizes of the two molecules are similar. Tetraline is another molecule in which one of the two rings of naphthalene has been altered by substitution. The object of the present investigation was to study the Raman spectra of quinoline and tetraline in different states in order to find out the change in the Raman spectra which might take place with change of state and also the number of low-frequency Raman lines in each case.

The infrared spectra of the two substances in the liquid state and also in solution in different solvents have also been studied in order to find out the influence of environment on the spectra.

EXPERIMENTAL

The liquids, quinoline and tetralin supplied by the British Drug House, England, were of chemically pure quality. They were further purified by repeated distillation under reduced pressure before each exposure. The arrangements used to record the Raman spectra of the two compounds in the liquid state and in the solid state at -180°C were the same as those used by Biswas (1954). An iron arc spectrum was superimposed on each spectrogram for comparison. The polarisation of Raman lines of tetralin was studied in the usual way. A Fuess glass spectrograph having a dispersion of $11\text{\AA}/\text{mm}$ in the 4047\AA region was used to photograph the spectra on Ilford Zenith plates. The infrared absorption spectra of the two compounds in the liquid state and in solution in CS_2 , CCl_4 and *n*-heptane have been recorded with a Perkin Elmer Model 21 spectrophotometer with NaCl optics. A compensation cell was used in the reference beam in each case.

RESULTS

The spectrograms are reproduced in Figs. 1, 2, and 3, Plate XI. The observed Raman shifts of the compounds in the liquid state and in the solid state at -180°C are tabulated in Tables I and III respectively. The Raman shifts for the corresponding liquids reported by previous workers are also included in the tables for comparison. The totally polarised and depolarised lines are indicated by the letters P and D respectively written by the side of each Raman line in Table III.

The infrared spectra of quinoline in the liquid state and its solutions in CS_2 and in CCl_4 are reproduced in Figs. 4, 5(a) & (b) and 6, respectively. Also, the infrared spectra of tetralin in the liquid state and of its solutions in CS_2 and in CCl_4 are reproduced in Figs. 7, 8 and 9(a) & (b) respectively. The infrared bands of pure quinoline and its solutions in CS_2 and in CCl_4 and those of pure tetraline and its solutions in CS_2 and in CCl_4 are tabulated in Tables II and IV respectively. The wave numbers of the bands of the pure liquids given in Landolt-Bornstein Tables are also included in the respective tables for comparison.

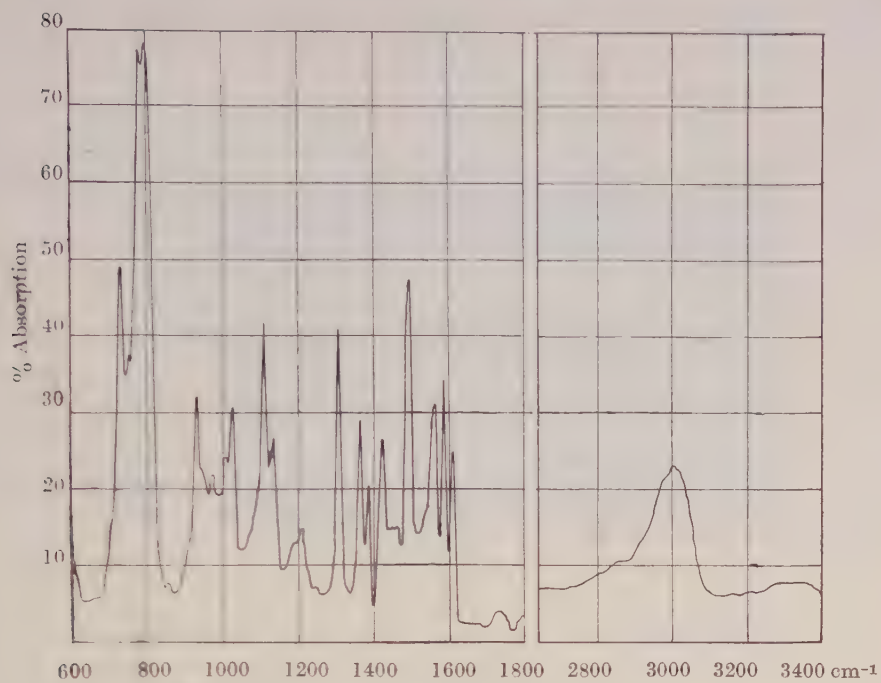
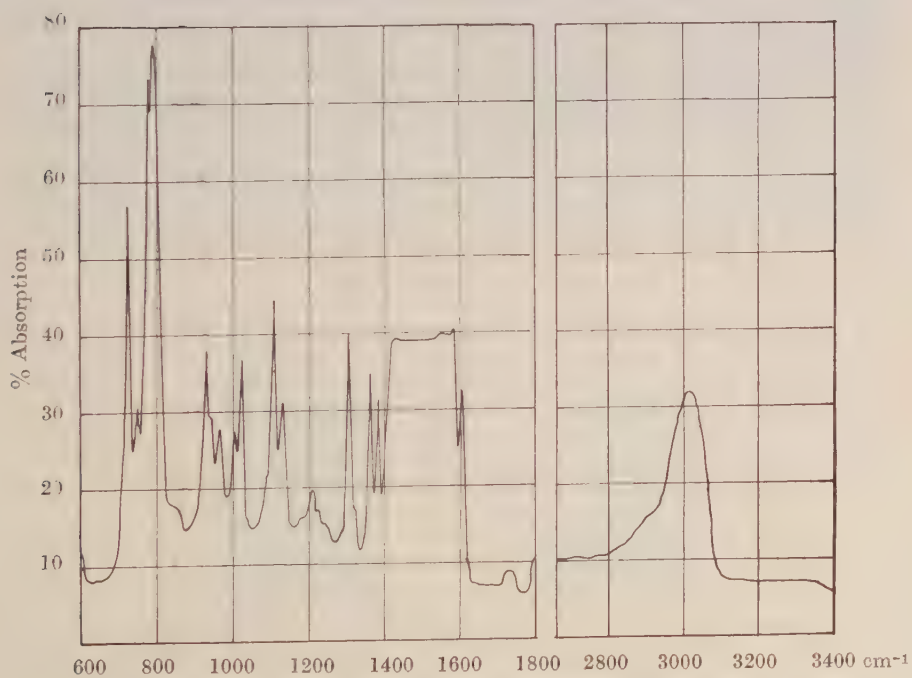


Fig. 4. Infrared spectrum of quinoline (liquid at 26°C).

Fig. 5(a) Infrared spectrum of 5% solution of quinoline in CS₂ (cell .05 mm)

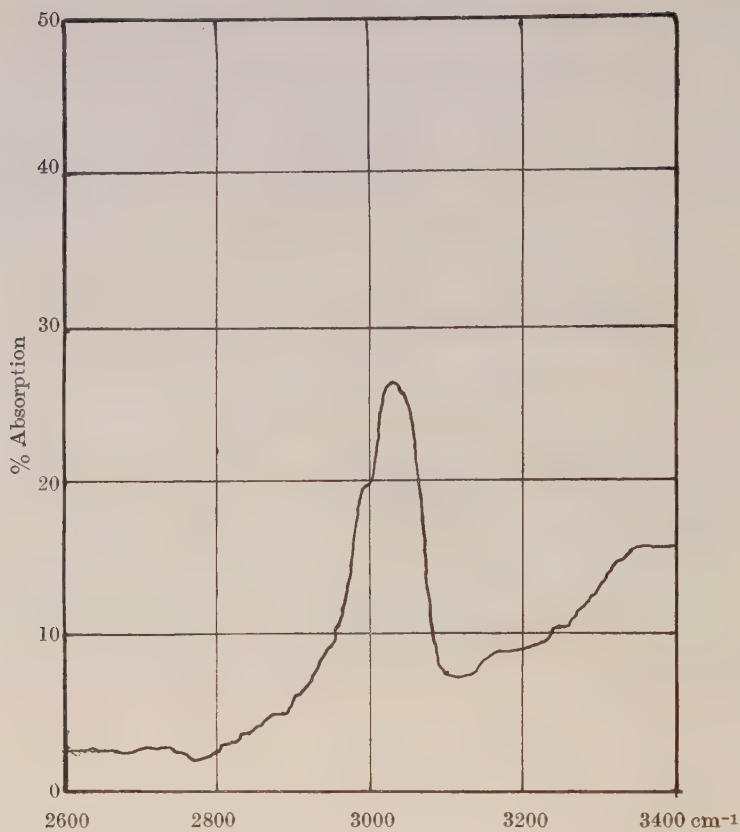


Fig. 5(b). Infrared spectrum of 15% solution of quinoline in CS₂ (cell .05 mm).

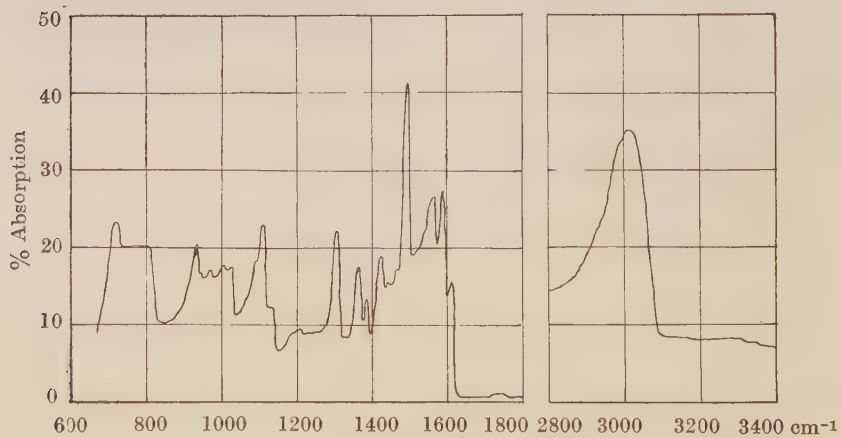


Fig. 6. Infrared spectrum of 5% solution of quinoline in CCl₄.



Fig. 1. (a) Raman spectrum of quinoline, liquid at 30°C
(b) " " " " quinoline, solid at -180°C
Fig. 2. (a) " " " " tetralin, liquid at 30°C
(b) " " " " tetralin, solid at -180°C
Fig. 3. (a) Low frequency band of quinoline at -180°C
(b) Low frequency Raman lines of tetralin at -180°C



TABLE I
Raman spectra of quinoline— $\Delta\nu$ in cm^{-1}

Liquid		Solid at -180°C
Landolt-Bornstein Tables (1951)	Present author	Present author
		49 (2b)
	191 (4b)	190 (2b)
388 (1)	386 (4)	384 (0)
518 (5)	519 (8)	516 (6)
701 (0)		
729 (1)		
755 (3)	757 (10)	751 (6)
771 (1)	776 (1)	
949 (1)		
975 (0)	963 (1b)	
1008 (2)	1013 (2)	1014 (0)
1028 (2)	1032 (6)	1030 (3)
1113 (1)	1117 (1)	
1137 (1)	1143 (2)	
1248 (1)		
1337 (0)	1310 (1)	
1367 (6)	1366 (15)	1366 (12)
1388 (2)	1390 (4)	1392 (1)
1428 (3)	1427 (10)	1428 (4)
1460 (1)	1464 (1)	
1491 (1)	1494 (1)	
1568 (4)	1572 (10)	1571 (4)
1589 (1)	1594 (1)	
1615 (0)	1628 (1)	
	2980 (0b)	
3011 (1)	3009 (1b)	
	3052 (4)	
3062 (3b)	3060 (6)	3088 (2Vb)
	3072 (2)	

TABLE II
Infrared spectra of quinoline— ν in cm^{-1}

Pure liquid		5% Solutions (Present author)	
Landolt-Bornstein Tables (1951)	Present author	in CCl_4	in CS_2
	730 ms	720 ms	730 ms
	755 ms		755 w
782 vs	782 vs		780 vs
800 vs	800 vs		798 vs
932 s	932 ms	932 ms	930 ms
950 s	950 vw		945 w
975 ms	975 vw	950 vw	970 w
1005 ms	1010 w	970 w	1010 w
		1005 w	
1030 s	1030 ms	1030 vw	1025 w
1090 vw	1090 vw	1090 vw	1090 vw
1110 vs	1110 s	1110 ms	1110 ms
1135 vs	1135 w	1135 vw	1135 w
1185 vw	1185 vw		
1210 vw	1210 vw	1210 vw	1210 vw
	1230 vw	1235 w	
1310 s	1310 s	1310 ms	
	1365 ms	1365 ms	1365 ms
1370 ms (b)	1390 w	1390 vw	1390 w
1427 s	1427 ms	1430 ms	1430 ms
1450 w	1450 vw	1445 vw	
1465 w	1465 vw	1465 vw	
1495 vs	1495 s	1498 s	
1540 vw	1540 vw	1542 w	
1565 ms	1565 ms	1560 ms	
1590 ms	1588 ms	1590 ms	
1615 ms	1610 ms	1610 w	
	1718 vw	1718 vw	1730 w
	1835 vw	1835 vw	1830 vw
	1860 vw	1860 vw	1870 vw
	1900 w	1820 w	1890 w
	1918 w		1920 w
	1950 w	1950 w	1950 w
	2230 vw		
	2270 vw		2290 w
	2310 w	2305 w	
	2340 vw		
	2840 vw	2415 vw	
*2890 w	2900 vw		
*2930 w			
*2950 ms			
	2980 s		
*3002 ms	3000 s	2995 ms	2995 ms
*3040 s	3025 s	3025 s (b)	3025 s (b)
*3080 s			

*Bands observed in solution in CCl_4

TABLE III
 Raman spectra of tetralin— $\Delta\nu$ in cm^{-1}

Liquid		Solid at -180°C
Landolt-Bornstein Table (1951)	Present author	Present author
		61 (2)
		92 (8)
113 (5)	107 (4) D	107 (2)
		137 (2)
163 (6b)	161 (8b) D	168 (4)
265 (4)	262 (4) P	265 (1)
311 (1)		
435 (6)	433 (6) P	432 (2)
457 (4)	458 (1) D	456 (0)
511 (4)	508 (4) P	
584 (6)	578 (6) P	578 (3)
725 (8)	722 (12) P	721 (10)
768 (1)		
805 (3)	804 (2)	804 (0)
816 (4b)	819 (2) D	819 (2)
866 (3)	869 (0) D	
905 (2)	915 (1) P	
982 (1)		
1037 (10)	1039 (12) P	1040 (8)
1067 (4)	1064 (1b) D	1064 (0)
1116 (1)		
1159 (6)	1162 (4) D	1162 (2)
1202 (8)	1205 (8) P	1206 (6)
1237 (3)	1236 (2) D	1236 (0)
1284 (3)	1280 (8) D	1281 (6)
1343 (4)	1337 (4b) P	
1381 (1)	1381 (1b) P	
1433 (6)	1432 (6) D	1427 (5)
1449 (3)	1452 (2)	
1581 (4)	1576 (2) D	1576 (0)
1603 (6)	1603 (8) D	1603 (6)
2836 (5)	2832 (6) P	2832 (3)
2864 (6)	2855 (3) P	2858 (2)
	2878 (3)	2878 (2)
2906 (5)	2907 (4)	2923 (4)
2923 (4)		
2939 (6b)	2930 (10) P	2932 (1)
		2953 (2)
3023 (3)	3025 (5b)	3025 (2)
	3055 (5b) P	
3045 (7)		3064 (3)

 TABLE IV
 Luminescence spectra in the solid state at -180°C — ν in cm^{-1}

Centres of the bands	Intensity	Separation between the two strong bands and two weak bands
23690	strong	1651
23583	weak	
22039	strong	
21933	weak	1650

TABLE V
Infrared spectra of tetralin, ν in cm^{-1}

Pure liquid		5% Solutions Present author		Solutions Landolt- Bornstein Table (1951)
Lambert and Le Comte (1938) & Wall and McMillan (1940)	Present author	in CCl_4	in CS_2	in CS_2
				580 s 620 ms 650 ms 670 ms 700 ms 740 s 780 s 805 s
740 s	735 vs 780 w 800 ms 810 w	730 ms 810 vw	735 vs 775 w 800 ms 810 w	
860 w	860 vw		855 w	855 w
905 w	895 w 940 ms 980 vw 1000 vw 1030 w 1060 w	890 w 938 w 980 vw 1000 vw 1030 w 1060 w	890 vw 940 ms 980 vw 1000 vw 1025 w 1060 w	890 ms 1025 ms 1055 ms
1111 w	1105 xw 1130 vw 1155 vw 1240 w 1280 ms 1330 w 1350 w	1105 vw 1238 w 1280 w 1350 vw	1100 w 1130 w 1150 w 1240 w 1280 ms 1330 w 1350 w	1102 s 1125 ms 1255 ms
1429 w	1430 ms	1430 s	1425 s	1435 s
1448 s	1445 s 1470 ms 1490 s 1575 vw 1598 vw 1630 vw 1640 vw	1450 s 1475 vs 1490 s 1575 vw	1470 vw 1490 vw 1570 w	
	1660 vw 1680 vw 1760 w 1800 w 1910 w 1940 w 2835 s 2890 s	1660 vw 1675 vw 1750 vw 1800 w 1902 w 1935 vw	1658 vw 1675 vw 1800 w 1905 vw 1930 vw 2835 ms	
2898 s	2900 s	2888 s 2900 s	2890 s 2900 s	
2975 ms	2985 ms	2985 ms	2985 ms	
3021 ms	3040 ms	3040 w	3040 w	
3058 w	3060 w	3060 w	3060 w	

DISCUSSION OF RESULTS

Quinoline(a) *Comparison with previous work*

Table I shows that almost all the Raman frequencies given in the Tables by Landolt and Bornstein agree with those observed in the present investigation excepting the fact that the lines 191 cm^{-1} , 2980 cm^{-1} were not reported by the previous workers and the feeble lines 701 , 729 , 1248 and 1337 cm^{-1} have not been observed in the present investigation. Of these the line 1248 cm^{-1} excited by 4047 Å line coincides with the antistokes line 519 cm^{-1} excited by the 4358 Å line. There is no indication of the other faint lines mentioned above in the spectrogram obtained in the present investigation. On the other hand, the broad lines 191 cm^{-1} and 2980 cm^{-1} are clearly visible on the spectrogram.

(b) *Assignment of some of the Raman lines*

The quinoline molecule is similar to the naphthalene molecule, the only difference being the absence of the centre of symmetry in the former molecule. The assignment of the vibrational frequencies of quinoline to the different fundamental modes was made earlier by Ichishima (1950). More recently, several attempts have been made to assign the frequencies of the naphthalene molecules. Lippincott and O'Reilly (1955) made such assignment by comparing the Raman and infrared frequencies of naphthalene and naphthalene *d*-8. The vibration frequencies of naphthalene have been calculated by Scully and Whiffen (1960) and those of planar vibrations of the molecule have been calculated by Freeman and Ross (1960). A comparison of the infrared and Raman spectra of quinoline with those of naphthalene may be helpful in arriving at the correct assignment of the frequencies of both the molecules, and therefore, an attempt is made here to compare these results.

Two of the nine A_g fundamentals of the naphthalene molecule given by Lippincott and O'Reilly (1955) do not agree with the corresponding frequencies given by Scully and Whiffen. These are 1240 cm^{-1} and 878 cm^{-1} . These fundamentals should appear as strong Raman lines and their frequencies for quinoline are expected to be very near to those of the naphthalene molecule. Table I shows that quinoline produces intense Raman lines corresponding to fundamental frequencies 519 , 557 , 1032 , 1366 , 1427 , 1572 and 3060 cm^{-1} . These agree fairly well with the corresponding frequencies of *g*-class vibrations of the naphthalene molecule given by Scully and Whiffen (1960). As regards the remaining two frequencies of naphthalene of this class, they have given them as 3025 cm^{-1} and 1144 cm^{-1} , while Freeman and Ross (1960) have given them as 3004 cm^{-1} and 1144 cm^{-1} . In the case of quinoline there is a weak line of Raman shift 3009 cm^{-1} and another line at 1143 cm^{-1} , but there is no line of Raman shift 3025 cm^{-1} . Hence the assignment of the A_g -class fundamentals of naphthalene made by Freeman and

Ross seems to be corroborated by the appearance of corresponding frequencies of A-class vibration in the Raman spectrum of quinoline. Some of the assignments made by Lippincott and O'Reilly therefore do not seem to be correct.

As the quinoline molecule has no centre of symmetry some of the modes which are antisymmetric to the centre of symmetry in the case of naphthalene and are forbidden in the Raman effect may appear as weak lines in the case of quinoline. The line 3072 cm^{-1} seems to be such a line. The infrared bands 1588 cm^{-1} and 1365 cm^{-1} of medium strength may correspond to the modes 1595 cm^{-1} and 1387 cm^{-1} of naphthalene. The strong band 1310 cm^{-1} is due to a vibration which is of *u*-class in naphthalene, because the mode appears also as a weak Raman line. This may correspond to a mode B_{1u} of frequency 1265 cm^{-1} given by Scully and Whiffen. There are two weak Raman lines of shifts 1628 cm^{-1} and 1594 cm^{-1} . There are no corresponding strong bands in the infrared. Hence these two lines are due probably to the modes corresponding to two B_{1g} modes of naphthalene numbered 16 and 17 by Lippincott and O'Reilly (1955).

Thus in the quinoline molecule some of the vibrations of the ring have frequencies very slightly different from those of the naphthalene molecule. This difference is evidently due to the presence of the C-N bond in place of a C-C bond in the ring.

(c) *Changes in the Raman spectra of solidification*

It is observed from Table I and Figs. 1(a) & (b) and 3(a) that quinoline in the solid state at -180°C does not exhibit numerous sharp low-frequency Raman lines unlike naphthalene (Sirkar and Ray, 1950) in the crystalline state. It produces only a moderately strong band with a Raman shift of 49 cm^{-1} on the Stokes side of the 4047 \AA line. It was observed earlier (Kastha, 1956) that pyridine in the solid state at -180°C produces four new low-frequency Raman lines, while benzene produces five such lines under similar conditions.

In the solid state at -180°C the Raman lines 3052 , 3060 and 3072 cm^{-1} coalesce to form a single broad line with its centre shifted to 3088 cm^{-1} . Also the Raman line 757 cm^{-1} corresponding to A-class vibration of quinoline shows a small shift towards the shorter wavelength region under similar conditions. All these changes suggest the formation of intermolecular linkage formed through hydrogen atoms of the neighbouring molecules in the solid state at -180°C .

(d) *Infrared spectra of solutions compared to the spectrum due to the pure liquid*

It can be seen from Table II that some bands given by previous authors appear to differ in intensity and position from those observed in the present investigation. The single broad band 1370 cm^{-1} given in Landolt-Bornstein Tables appears as a doublet at 1365 and 1390 cm^{-1} in the present investigation. It is observed from Figs. 4; 5(a) & (b) and 6 that the band 755 cm^{-1} becomes weak in the spectrum due to the dilute solution of quinoline in CS_2 . Moreover, the first

component of the triplet 2980 cm^{-1} , 3000 cm^{-1} and 3030 cm^{-1} due to pure quinoline seems to be weakened very much in 5% solutions in CS_2 and CCl_4 and it again appears weakly in 15% solution in CS_2 . This shows that quinoline molecules in the liquid state are probably strongly associated and the 2980 cm^{-1} band may be due to such associated molecules. The association thus breaks up in the dilute solution. The 757 cm^{-1} band corresponds to the Raman line of the same vibrational frequency, but the mode being of A-Class, it is forbidden in the infrared in the case of naphthalene. It appears weakly in the case of solution of quinoline in CS_2 probably because in this case the centre of symmetry is disturbed by the presence of the nitrogen atom in the ring. The fact that the strength of the band increases in the pure liquid clearly shows that the centre of symmetry is perturbed to a greater extent and this also may be due to intermolecular coupling in the pure liquid mentioned above.

It can be seen from Table II that there is no strong infrared band due to C-H vibration of frequency greater than 3025 cm^{-1} , although naphthalene shows a strong band at 3072 cm^{-1} . The band at 3025 cm^{-1} is to be assigned to a mode corresponding to a mode of u -class of naphthalene. It may correspond to the second B_{2u} mode listed by Scully and Whiffen (1960). The strong bands 782 cm^{-1} and 800 cm^{-1} may be assigned to modes corresponding respectively to mode No. 7 of B_{1u} class and No. 7 of B_{2u} class given by Freeman and Ross (1960).

Tetralin

(a) Comparison with previous work

It is observed from Table III that the doublet 2923 and 2939 cm^{-1} reported by previous workers are not resolved in the present investigation and only one broad line 2930 cm^{-1} has been observed. An extra line 2878 cm^{-1} is also present in the spectrogram obtained in the present investigation. Regarding the other Raman lines the agreement is good excepting the lines 768 and 982 cm^{-1} which are not present in the spectrogram.

(b) Changes in the Raman spectra on solidification

It can be seen from Table III and Fig. (3b, 2a and 2b) that tetralin in the solid state at -180°C produces two new low-frequency Raman lines of shifts 67 cm^{-1} and 92 cm^{-1} respectively. Of these the line 92 cm^{-1} is stronger than the former one. It was previously observed (Sirkar and Ray, 1950) that naphthalene in the crystalline state produces six such lines under similar conditions. Similar comparison of the spectra due to benzene and cyclohexane shows that benzene produces five low frequency Raman lines (Sirkar and Ray, 1950) while cyclohexane does not produce any low frequency Raman line (Sirkar and Gupta, 1937). It thus appears that the presence of the six unsaturated π -electrons is necessary for the production of the low frequency lines in the case of compound

containing carbon rings. Tetralin may be regarded as a modified molecule of naphthalene with a cyclohexane ring attached to a benzene ring. Hence the diminution in the number of low frequency Raman lines in the case of the solidified tetralin at -180°C may be attributed to the diminution in the number of benzene rings in the molecule.

(c) *Other changes in the Raman spectra*

It can be seen from Table III that the Raman line 161 cm^{-1} which probably corresponds to a B_{3u} mode in naphthalene (Scully and Whiffen, 1961) is split up into two lines 137 cm^{-1} and 168 cm^{-1} respectively when the compound is solidified and cooled to -180°C . The Raman line 1432 cm^{-1} which is due to C-H bending mode also shows a small shift towards the shorter wavelength region in the solid state at -180°C . The line 2907 cm^{-1} shifts to 2923 cm^{-1} and the line 2930 cm^{-1} which is due probably to aromatic C-H stretching mode is split up into two components at 2932 and 2963 cm^{-1} with the solidification of the liquid. Further, the line 3055 cm^{-1} shifts to 3064 cm^{-1} at the low temperature. On the other hand, the lines 2832 , 2855 and 2878 cm^{-1} remain unchanged at the low temperature. This shows that the C-H stretching vibrations in the CH_2 group remain unaffected while these due to C-H group in the ring undergo changes with solidification.

These changes suggest that probably some weak intermolecular coupling is formed in the frozen state of the substance at -180°C and the low-frequency lines may also be attributed to such coupling.

(d) *Luminescence spectra*

It can be seen from Figs. 3a and 3b that tetralin in the liquid state exhibits strong continuous luminescence, which with lowering of temperature at -180°C , appears as four discrete bands with centres at about 21933 , 22039 , 23583 and 23690 cm^{-1} respectively as shown in Table IV. In the case of quinoline, no such bands have been observed in the solid state at -180°C . The separations of the two strong bands and two weak bands are 1651 and 1650 cm^{-1} respectively. This difference may correspond to the wave number 1680 cm^{-1} assigned to a B_{3u} mode of naphthalene (Lippincott and O'Reilly, 1955). Probably, this type of vibration makes the triplet \rightarrow singlet electronic transition partially allowed, so that the emission of the fluorescence bands takes place in the solid state at -180°C .

(e) *Infrared spectrum of solutions compared with the spectrum due to pure liquid*

Table V shows that the infrared bands due to pure tetraline reported by previous workers agree closely with those observed in the present investigation. It can also be seen from Table V that some of the infrared bands of solution of the liquid in CS_2 observed by previous workers differ in intensity and position from those observed in the present work. Instead of the medium strong band 1255 cm^{-1} reported in Landolt-Bornstein Tables (1951), two weak bands 1240 cm^{-1}

and 1280 cm^{-1} have been observed in the present work. Also the relative strengths of the absorption bands 855 and 890 cm^{-1} reported in the Table seem to be reversed.

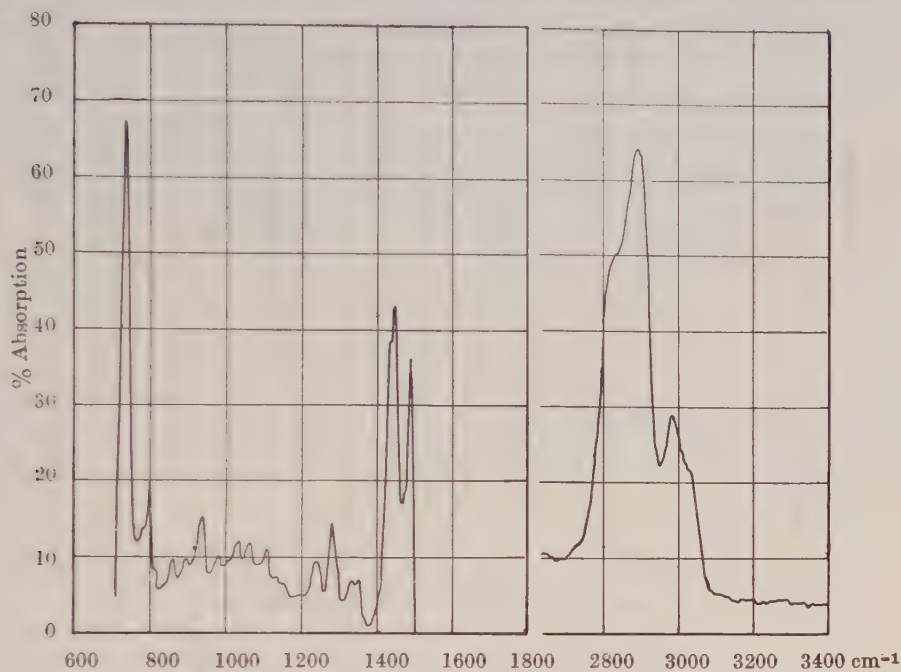


Fig. 7. Infrared spectrum of tetralin (liquid at 27°C.)

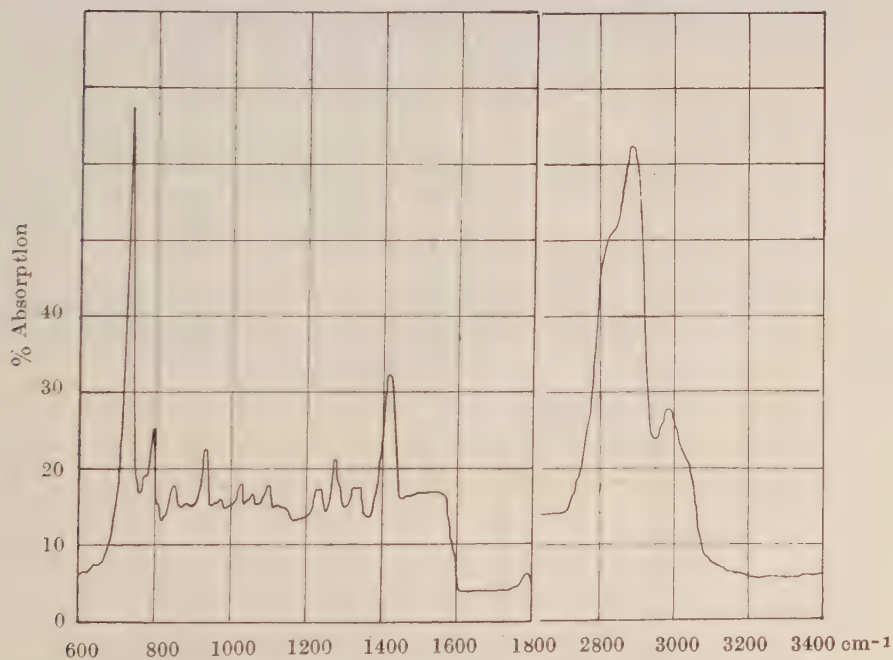


Fig. 8. Infrared spectrum of 5% solution of tetralin in CS_2 (cell .05 mm.)

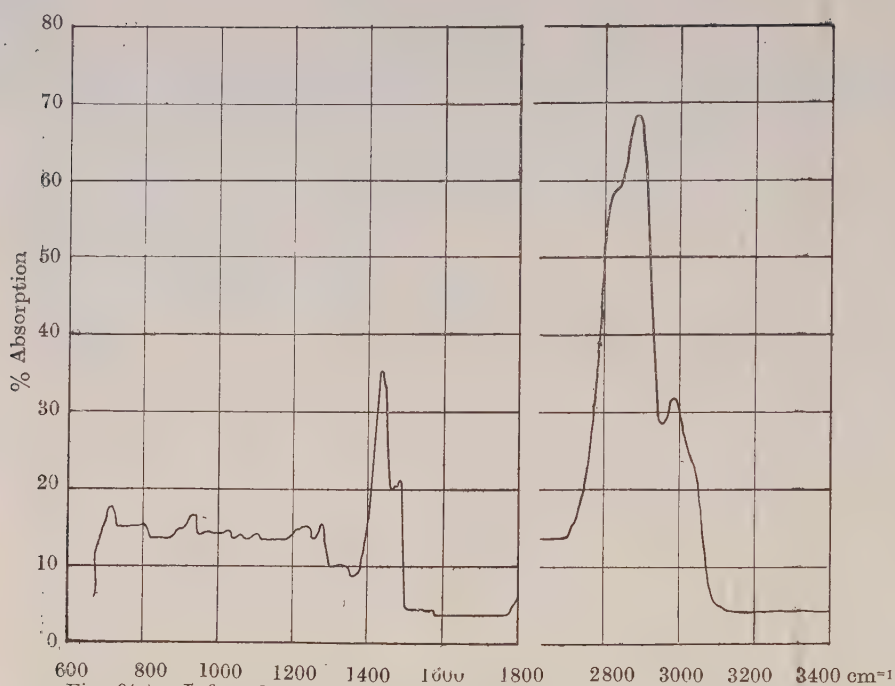


Fig. 9(a). Infrared spectrum of 5% of tetralin solution in CCl_4 (cell 0.5 mm).

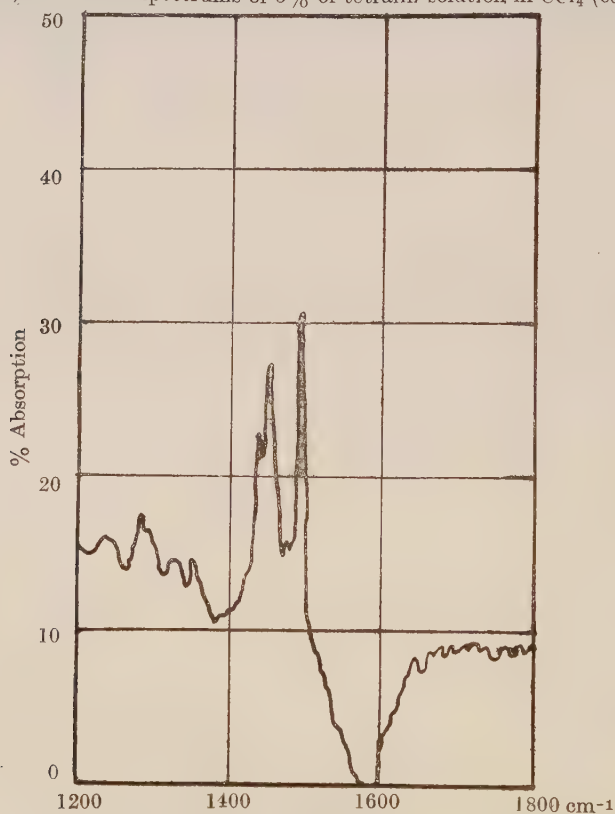


Fig. 9(b). Infrared spectrum of 5% solution of tetralin in CCl_4 (cell .02 mm).

It is observed from Figs. 7 and 9(a) & (b) that the relative strengths of the bands 1490 cm^{-1} and 1445 cm^{-1} corresponding to C-H bending modes change considerably when the substance is dissolved in CCl_4 , the band 1490 cm^{-1} being stronger than the band 1445 cm^{-1} in the spectrum due to the solution while it is weaker in the spectrum due to the pure liquid. Also the bands 2835 and 2985 cm^{-1} , which correspond respectively to the hydrogen stretching modes in CH_2 and C-H groups slightly increase in strength when the substance is dissolved in CCl_4 . No such change is observed in the case of solution in CS_2 . So, it appears that the chlorine atoms of the solvent have some influence on the absorption due to C-H valance oscillations.

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ON THE CALCULATION OF LOW-ENERGY NEUTRON SCATTERING BY A COMPLEX POTENTIAL

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ABSTRACT. The scattering of low-energy neutrons by a potential $V(r) = -(V + iW)[1 + e^{(r-R)/a}]^{-1}$ is calculated by applying a method of Lanczos (1938) for solving the Schrödinger equation. The neutron strength function $\overline{\Gamma}_n^0/D$ which is the ratio of the average value of neutron width to level spacing is obtained from the scattering amplitude. That this analytic method of solution is fairly exact is borne out by the fact that our results agree closely with the finding of Feshbach, Porter and Weisskopf (1954) who have solved numerically the differential equation with the same potential.

INTRODUCTION

A number of investigations (Feshbach *et al.*, 1954; Feshbach, 1958) have been made in interpreting the interaction of slow neutrons with a nucleus taking the nuclear potential to be complex. The resonance structure of neutron strength function has been first discussed by Feshbach, Porter and Weisskopf (1954) and they calculated the strength function with a complex square well potential. Later on Feshbach (1958) have solved numerically the Schrödinger equation with the Woods-Saxon potential and the results so obtained have nearly the same general pattern as those of the complex square well. The agreement with experimental findings is fair, Feshbach obtained for the value of $\overline{\Gamma}_n^0/D$ at $A = 155$, one maximum whereas the experimental results indicate two small peaks.

The object of the present paper is to solve analytically the Schrödinger equation with the Woods-Saxon potential for the case of positive energy states, the method employed here is due to Lanczos (1938) which we have already applied to solve the bound state problem (1960). Previously Lawson (1956) has obtained a solution of this problem in the form of infinite series the terms of which converge very badly, as such the solution of Lawson is not so useful in its application to physical problems. In our case if we take the solution up to eighth term the error in the differential equation is of the order of 1 in 10^6 . Our results agree well with similar ones of Feshbach (1958).

In the theory of Feshbach, Porter and Weisskopf (1954) it is shown that for

very low energy neutrons the scattering amplitude averaged over resonances is given by

$$\bar{\eta}_0 = e^{-2iKR'}(1 - \pi\bar{\Gamma}_n/D) \quad \dots (1)$$

This gives $\bar{\Gamma}_n/D$ which is the ratio of the average value of neutron width to level spacing and R'/R where R' has the dimension of length and is a slowly varying function of energy. The magnitude of R' is of the order of nuclear dimension and it plays the role of scattering length; K is $\left(\frac{2M}{\hbar^2} E\right)^{1/2}$. The average total cross section (Feshbach *et al.*, 1954) is

$$\begin{aligned} \sigma_t^{(0)} &= \frac{\pi}{K^2} \{ |1 - \bar{\eta}_0|^2 + 1 - |\bar{\eta}_0|^2 \} \\ &= 4\pi R'^2 + \frac{2\pi^2}{K^2} \bar{\Gamma}_n/D \quad \dots (2) \end{aligned}$$

MATHEMATICAL FORMULATION AND RESULTS

The interaction potential between the neutron and the nucleus is taken as

$$V(r) = -(V + iW)[1 + e^{(r-R)/a}]^{-1}$$

where R is a measure of the nuclear size and a is the diffusivity parameter. The Schrödinger equation for $l = 0$, scattering with the above potential may be written as

$$\frac{d^2u}{dx^2} + \frac{\lambda^2}{1 + \beta e^x} u + K'^2 u = 0 \quad \dots (3)$$

where $x = r/a$; $K'^2 = \frac{ZM}{\hbar^2} E a^2$; $\lambda^2 = \frac{2M}{\hbar^2} (V + iW) a^2$; $\beta = e^{-R/a} = e^{-x_0}$

The wave function $u = r\psi$ satisfies the necessary boundary conditions for scattering at $x=0$ and $x \rightarrow \infty$.

In the region $R \leq r < \infty$ we may write the solution as

$$u^0(x) = e^{-iK'x} F_- - \bar{\eta}_0 e^{iK'x} F_+ \quad \dots (4)$$

where $\bar{\eta}_0$ is the scattering amplitude averaged over neutron resonance energies.

We now make a transformation of the independent variable from x to $p = e^{-(x-x_0)}$ such that the new independent variable varies from 0 to 1. Then F_{\pm} satisfies the differential equation

$$\begin{aligned} D_{\pm}(F_{\pm}) &= 0, \\ D_{\pm}(F_{\pm}) &\equiv p(p+1) \frac{d^2 F_{\pm}}{dp^2} + (p+1)(1 \mp 2iK') \frac{dF_{\pm}}{dp} + \lambda^2 F_{\pm} \end{aligned}$$

Applying the suggestion of Lanczos (1938) we now modify the differential equation by equating it to an error term proportional to Tshebysheff's polynomial $T_n(p)$ instead of to zero,

$$D_{\pm}(F_{\pm}) = \tau_{\pm} T_n(p) \quad \dots (5)$$

$$\text{Let} \quad T_n(p) = B_0 + B_1 p + B_2 p^2 + \dots + B_n p^n \quad \dots (6)$$

Now we put the finite series

$$\overline{F}_{\pm} = a_0 + a_1 p + a_2 p^2 + \dots + a_n p^n \quad \dots (7)$$

in the differential Eq. (5) and comparing the coefficients of the same power of p on both sides of the equation we get the recursion formulae

$$\begin{aligned} \tau_{\pm} B_r &= a_r \pm [\lambda^2 + r(r \mp 2iK')] + a_{r+1} \pm [(r+1)(r+1 \mp 2iK')], \\ \tau_{\pm} B_n &= a_n \pm [\lambda^2 + n^2 \mp 2iK'n] \end{aligned} \quad \dots (8)$$

These relations will determine the coefficients a_r of the approximate solutions and the factor τ_{\pm} which estimates the error of the approximation in terms of a_0 .

In the region $0 < r \leq R$ we write the solution as

$$u^i(x) = e^{i\gamma x} f_+ - e^{-i\gamma x} f_- \quad \dots (9)$$

where

$$\gamma = \sqrt{\lambda^2 + K'^2};$$

We make a transformation of the independent variable from x to $q = (e^x - 1)/(e^{x_0} - 1)$ such that the new independent variable varies from 0 to 1. Then f_{\pm} satisfies the differential Eq.

$$q(q+1) \frac{d^2 f_{\pm}}{dq^2} + (q+1)(1 \pm 2i\gamma) \frac{df_{\pm}}{dq} - \lambda^2 f_{\pm} = 0 \quad \dots (10)$$

(neglecting terms involving $\beta \approx 10^{-6}$) we take

$$f_{\pm} = b_0 + b_1 p + b_2 p^2 + \dots + b_n p^n \quad \dots (11)$$

and get as before the recursion formulae to determine b_r and τ_{\pm}' which estimates the error in terms of b_0 .

$$\begin{aligned} \tau'_{\pm} B_r &= b_r \pm [-\lambda^2 + r(r \pm 2i\gamma)] + b_{r+1} \pm [(r+1)(r+1 \pm 2i\gamma)] \\ \tau'_{\pm} B_n &= b_n \pm [-\lambda^2 + n(n \pm 2i\gamma)] \end{aligned} \quad \dots (12)$$

From the continuity of the solution u and its derivative we obtain

$$\overline{\eta}_0 = e^{-2iK'x_0} \left[\frac{[(AG - CE)e^{2i\gamma x_0} + (CF - AH)]}{(BG - DE)e^{2i\gamma x_0} + (DF - BH)} \right] \quad \dots (13)$$

where

$$A = \sum_{r=0}^n a_r^- \quad B = \sum_{r=0}^n a_r^+$$

$$C = -iK'A - \sum_{r=1}^n r a_r^-$$

$$D = iK'B - \sum_{r=1}^n r a_r^+$$

$$E = \sum_{r=0}^n b_r^+; \quad F = \sum_{r=0}^n b_r^-$$

$$G = i\gamma E + \sum_{r=1}^n r b_r^+; \quad H = -i\gamma E + \sum_{r=1}^n r b_r^-;$$

From equations (1) and (13) we obtain the expression for $\bar{\Gamma}_n/D$ and R'/R which are calculated with the following values of the parameters $V_0 = 52\text{ MeV}$; $W = 3.12\text{ MeV}$; $R = (1.15A^{1/3} + 0.4)10^{-13}\text{ cm}$, $a = 0.57 \times 10^{-13}\text{ cm}$. The parameters are the same as taken by Feshbach *et al.* (1958) who obtained the neutron strength function by numerically solving the Schrödinger equation with the same potential. The curves of $\bar{\Gamma}_n/D$ (normalised to 1 ev) and R'/R are plotted against mass number

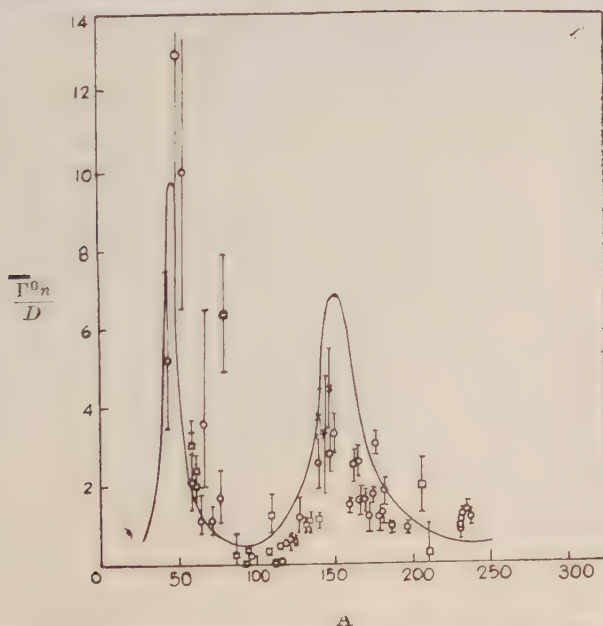


Fig. 1. Ratio $\bar{\Gamma}_n^0/D$ of neutron width to level spacing. Here $\bar{\Gamma}_n^0/D$ is normalized to 1 ev.

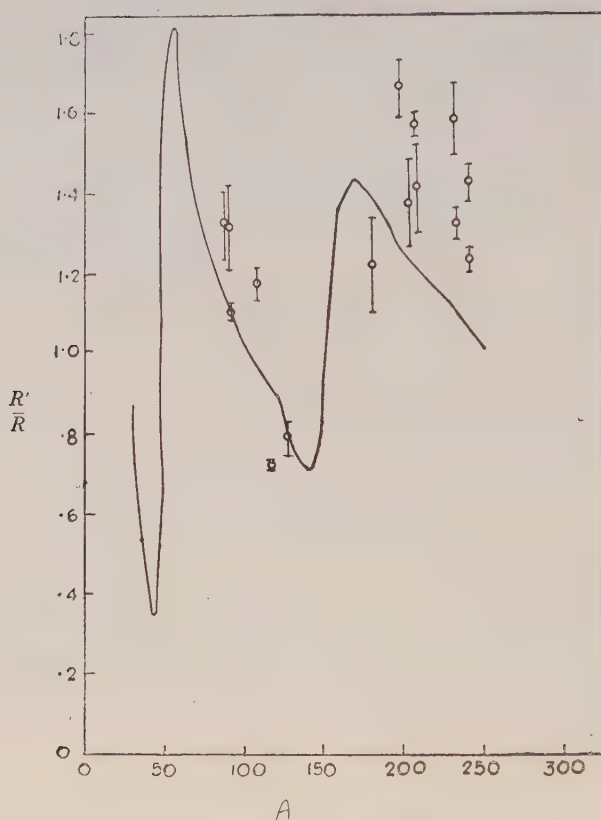


Fig. 2. Ratio of potential scattering length R' to nuclear radius R .

in Fig. 1 and Fig. 2 and compared with the experimental results. In the experiment the minimum in $\bar{\Gamma}_n^0/D$ between the two resonances is deeper than the theory predicts and the peak at $A = 155$ is much broader, lower and irregular than that of the calculated curve. A better fit of $\bar{\Gamma}_n^0/D$ at $A = 155$ has been obtained by Margolis *et al.* (1957) who has replaced the spherical square well by a spheroidal square well with the idea that the nuclei in this region are not spherically symmetrical. Similarly, in the R'/R curve closer agreement with the experimental results may be obtained for nuclei with $A = 200$ if the deformation of these nuclei is taken into account. In our curve of $\bar{\Gamma}_n^0/D$ the two maxima occur at $A = 48$ and 155 whereas in the calculation of Feshbach (1958) they occur at $A = 55$ and 155. Except for this shift of the peak point the two curves agree closely. The value of R'/R at about $A = 43$ is minimum in both the cases, but our value is numerically higher than that of Feshbach (1958); in all other regions the agreement between the two is good. Unfortunately there is no experimental result in the region $A = 43$ to indicate which one is superior to the other. In Fig. 3 we present for different elements the average total cross section (sum of elastic scattering and nuclear reactions) of neutrons of energy 500 eV in the unit of πR^2 .

The series solution given here has the advantage that the number of terms to be taken in the polynomial is determined by the degree of accuracy one desires in

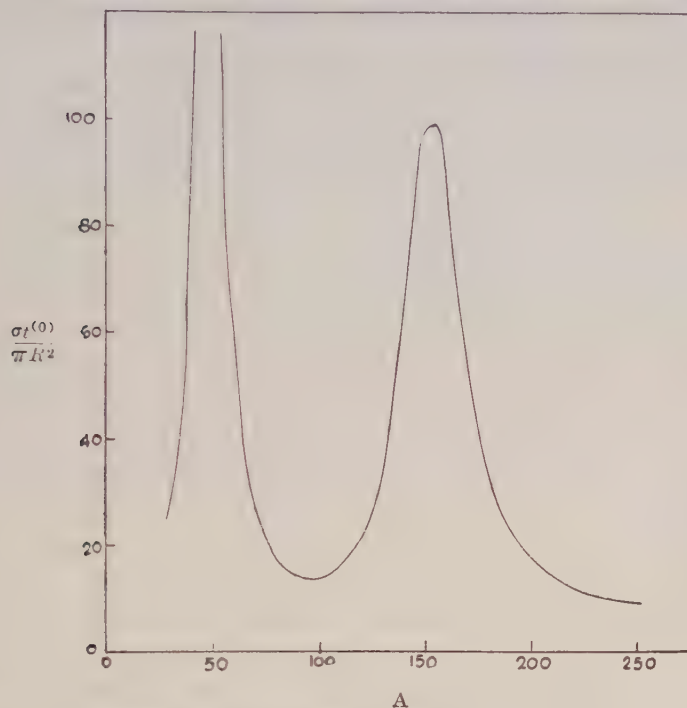


Fig. 3. Calculated total cross section of neutrons as a function of mass number.

the differential equation. For an accuracy of 1 in 10^6 in the differential equation it is sufficient to take a polynomial of the order of 8 whereas it is necessary to take several times this number of terms to achieve the same accuracy in Lawson's (1956) series.

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THE SPECTRUM OF CoCl IN THE PHOTOGRAPHIC INFRARED AND THE VISIBLE

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Plate XII A & B

ABSTRACT. The spectrum of CoCl has been examined in the photographic infrared and the visible using both low and high dispersion. Several new brief systems have been observed in the visible region λ 4600— λ 5100 Å, and in the photographic infrared region λ 6850— λ 7950 Å. Vibrational constants of the various systems have been derived from the analyses. The new systems, designated in this paper as F, G, H, I are observed to consist of single headed bands while the remaining systems J, K, L, N_1 , N_2 and O are observed to be double headed. It is suggested that the two systems N_1 and N_2 in the photographic infrared might belong to two components of a $^3\Pi$ — $^3\Sigma$ transition.

INTRODUCTION

The band spectrum of cobalt chloride has been investigated by several earlier workers, Mesnage (1935), More (1938), and Krishnamurty (1952). On the basis of high dispersion spectrograms, taken in the second order of a 21 ft. concave grating spectrograph, More (1938) gave vibrational analyses of three systems designated by him as 1, 2 and 3 in the region (λ 4200— λ 4750 Å). The bands in each of the three systems are single-headed and degraded to longer wavelengths. Recently, Krishnamurty has identified two more systems, designated as 4 and 5 in the same spectral region. These consist also of bands degraded to longer wavelengths. In addition, Krishnamurty proposed the vibrational analyses of six groups of line-like bands slightly degraded to red in the region (λ 5350— λ 6000 Å) on the basis of a $^5\Pi$ — $^5\Sigma$ transition. His analysis was however based on measurements of plates taken under low dispersion, (25—30 Å/mm).

In a previous paper (Rao *et al.*, 1961) we have reported the results of a study of the spectrum of NiCl in the photographic infrared under high dispersion. In continuation of this work we have examined the spectrum of CoCl in the photographic infrared and the visible, both under low and high dispersion. This work has disclosed the existence of a number of new band systems of CoCl in the photographic infrared region (λ 6850— λ 7950 Å), and in the visible region (λ 4600— λ 5100 Å). The structure and analyses of these new band systems are discussed in this paper.

EXPERIMENTAL

The spectra were excited both in a heavy current discharge from a 2000 volt d.c. generator and in a high frequency discharge from a 100 watt oscillator

using an anhydrous B.D.H. sample of CoCl_2 . The spectra were photographed under low dispersion on a Hilger three prism glass Littrow instrument (17 \AA/mm), and also in the first and second orders of a 21 ft. concave grating spectrograph (dispersion 2.5 \AA/mm and 1.25 \AA/mm) using appropriate filters. Exposures of two to five hours duration were found necessary for obtaining the spectra on the grating, using Kodak I.N. plates and Agfa Isopan plates. Second order iron arc lines were used as standards for measurements of all grating plates.

RESULTS AND ANALYSIS

All the five band systems observed and analysed by More (1938) and Krishnamurty, (1952) in the spectral region ($\lambda 4200\text{--}\lambda 4750 \text{ \AA}$) were photographed in the present work both under low and high dispersion. In the order of increasing wavelength, systems 3, 2, 4, 5 and 1 are designated as A, B, C, D, E respectively. The bands in each of the systems appear single headed and arise from a transition in which $\Delta \Lambda = 0$ in Hund's case 'a' or $\Delta \Omega = 0$ in Hund's case 'c'.

The six groups of line like bands (designated as *M* in this paper) observed and analysed by Krishnamurty in the region ($\lambda 5350\text{--}\lambda 6000 \text{ \AA}$) were too weak to be photographed under high dispersion and therefore they are not considered in the present work. In the spectrum of CoCl excited in a high frequency discharge from a 100 Watt oscillator we have observed a number of new band systems in the region ($\lambda 4600\text{--}\lambda 5100 \text{ \AA}$). According to our analyses, based on a close scrutiny of both low and high dispersion spectrograms, the bands of CoCl in this region were classified as belonging to seven separate brief systems. Each of these systems is characterised by a strong $\Delta v = 0$ sequence with weaker $\Delta v = -1$ or $+1$ sequence. In the order of increasing wavelength these were designated as *F*, *G*, *H*, *I*, *J*, *K* and *L* systems respectively. The bands in each of the systems *F*, *G*, *H* and *I* are single headed, degraded to red and interpreted as the *R* heads. The bands in *J*, *K* and *L* systems are double headed and interpreted as the *R* and *Q* heads. The data and classifications of these bands are given in Table I. Low dispersion spectrograms of these seven systems are shown in strips (a and b) in Plate XII A, Fig. 1. Grating spectrograms of the prominent bands of the strong $\Delta v = 0$ sequence in different systems are shown in strips (a, b and c) in Plate XII B, Fig. 2. In the bands of the weaker $\Delta v = \pm 1$ sequences only the heads of the more abundant Co^{35}Cl species could be identified.

In the spectrum of CoCl excited in a heavy current discharge from a 2000 volt D.C. generator we have observed two new systems of bands in the photographic infrared region ($\lambda 6850\text{--}\lambda 7960 \text{ \AA}$). The observed spectrum in the region ($\lambda 6850\text{--}\lambda 7200 \text{ \AA}$) taken under low dispersion can be seen from strip (c) in Plate XII A, Fig. 1, to consist of four characteristic groups of bands. Of these, two stronger groups beginning at $\lambda = 7117.0 \text{ \AA}$ and 7171.2 \AA are identified as the two $\Delta v = 0$ sequences of two components of a $^3\Pi\text{--}^3\Sigma$ transition. The weaker groups beginning at $\lambda = 6892.8 \text{ \AA}$ and $\lambda = 6941.2$ are identified as two $\Delta v =$

± 1 sequences respectively. The double headed nature of the bands of this system designated as $N(N_1$ and $N_2)$ can be seen clearly from grating spectrograms shown in strip (d) in Plate XII B, Fig. 2. The data and classification of the bands are given in Table II.

TABLE I
Band heads of CoCl in the region ($\lambda 4600$ — $\lambda 5100 \text{ \AA}$)

Wavenumber	Int.	Classification	Wavenumber	Int.	Classification
system—F			system—J		
21640.4	8	0,0	20358.4	7	1,0 R
21639.0	8	1,1	20356.4	5	1,0 Q
21230.5	5	0,1	20339.4	6	2,1 R
21228.2	5	1,2	20337.7	6	2,1 Q
21225.2	5	2,3	19950.9	9	0,0 R
system—G			19945.8	9	0,0 Q
21335.1	8	0,0	19927.5	8	1,1 R
21320.0	8	1,1	19925.1	8	1,1 Q
21306.0	8	2,2	system—K		
20933.1*	5	0,1	20279.6	5	1,0 R
20923.4*	5	1,2	20277.5	4	1,0 Q
20914.2*	5	2,3	20263.1	5	2,1 R
system—H			20260.3	5	2,1 Q
21263.9	10	0,0	19869.7	10	0,0 R
21257.1	7	1,1	19868.1	10	0,0 Q
21247.2	6	2,2	19851.9	8	1,1 R
20847.9*	3	0,1	19849.9	8	1,1 Q
20842.0*	4	1,2	system—L		
20832.7*	4	2,3	19829.5	9	0,0 R
20825.8*	4	3,4	19826.3	9	0,0 Q
system—I			19804.3	9	1,1 R
21372.5*	3	1,0	19801.2	9	1,1 Q
21365.2*	3	2,1	19781.2	7	2,2 R
21357.9*	3	3,2	19779.2	7	2,2 Q
20969.1*	7	0,0	*Measured on low dispersion plates only.		
20963.4*	5	1,1			

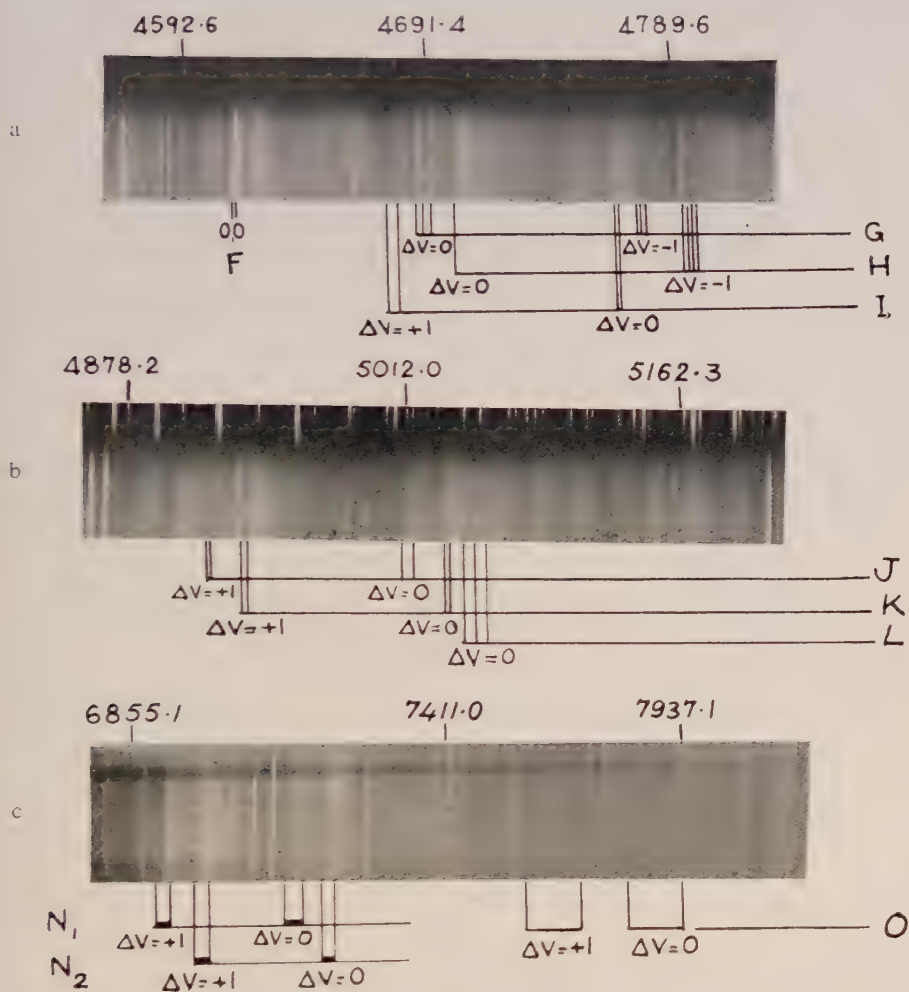


Fig. 1. New band systems of CoCl in the photographic infrared and the visible. (low dispersion spectrograms).

a — systems F, G, H and I.

b — systems J, K and L.

c — systems N_1 , N_2 and O.

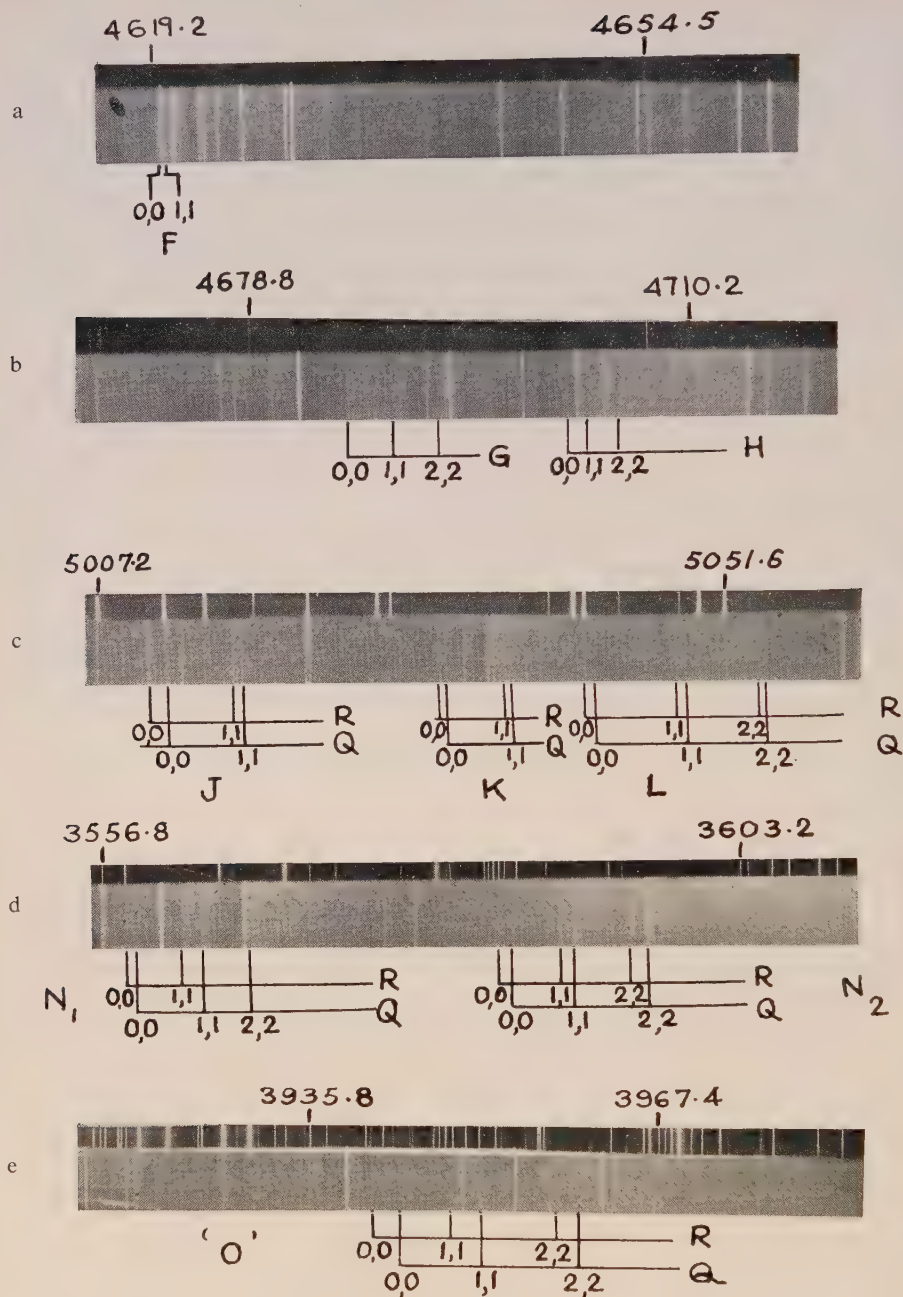


Fig. 2. New band systems of CoCl in the photographic infrared and the visible (21 ft. grating spectrograms).

- a — $\Delta V=0$ sequence of system F.
- b — $\Delta V=0$ sequence of systems G, H.
- c — $\Delta V=0$ sequence of systems J, K and L.
- d — $\Delta V=0$ sequence of systems N_1 and N_2 .
- e — $\Delta V=0$ sequence of system O.

In the region ($\lambda 7600\text{--}\lambda 7950\text{\AA}$) a weaker system (designated as 0) shown in strips (c) in Plate XII A, Fig. 1 and (e) in Plate XII B, Fig. 2, has been observed. The strong group beginning at $\lambda = 7882.4\text{\AA}$ is identified as the $\Delta v = 0$ sequence and the weaker group beginning at $\lambda = 7612.2\text{\AA}$ as $\Delta v = +1$ sequence. In the $\Delta v = 0$ sequence the *R* and *Q* heads are identified while in the weaker $\Delta v = -1$ sequence only *R* heads have been identified. The data and classifications of the bands are given in Table II. Table III summarizes the vibrational constants of the different band systems of CoCl.

TABLE II
Band heads of CoCl in the region ($\lambda 6850\text{--}\lambda 7950\text{\AA}$)

Wavenumber	Int.	Classification	Wavenumber	Int.	Classification
system—N ₁			system—O		
14503.9	4	1,0 R	13159.1	4	1,0 R
14501.4	4	1,0 Q	13130.8	5	2,1 R
14483.3	4	2,1 R	13098.8	5	3,2 R
14480.4	5	2,1 Q	12883.0	7	0,0 R
14461.5	6	3,2 R	12674.6	6	0,0 Q
14459.0	6	3,2 Q	12658.6	8	1,1 R
14047.0	3	0,0 R	12650.6	7	1,1 Q
14044.2	3	0,0 Q	12628.2	8	2,2 R
14031.2	5	1,1 R	12621.8	8	2,2 Q
14026.1	5	1,1 Q			
14012.4*	L	2,2 Q	*Superposed by atomic line.		
system—N ₂					
14402.8	4	1,0 Q			
14380.4	5	2,1 Q			
14389.7	5	3,2 Q			
13940.8	4	0,0 R			
13937.7	4	0,0 Q			
13924.1	5	1,1 R			
13920.3	7	1,1 Q			
13904.0	6	2,2 R			
13899.7	10	2,2 Q			

TABLE III

Summary of the vibrational constants of CoCl

System	Wave number of the (0,0) band	we'	$xe'we'$	we''	$xe''we''$
A	22966.2	420.0	1.66	421.8	1.34
B	22402.7	416.6	0.82	419.4	0.28
C	22182.5	401.0	—	416.2	—
D	22072.3	410.2	—	416.4	—
E	22014.8	420.0	1.14	421.2	0.74
F	21640.4	408.0	—	409.0	—0.45
G	21335.1	391.2	2.15	407.1	2.55
H	21263.9	413.2	2.00	416.8	0.38
I	20969.1	405.0	0.80	409.0	—
J	19945.8	408.6	—1.00	431.0	—
K	19868.1	408.4	—0.50	428.0	—
L	19826.3	—	—	—	—
M	17484.1	412.3	—	416.0	—
N ₁	14044.2	462.5	2.65	482.6	3.65
N ₂	13937.7	467.6	1.25	484.3	0.90
O	12683.0	478.8	1.38	498.4	—1.05

DISCUSSION

From the magnitude of the vibrational constants of the upper and lower states, More (1938) has suggested that systems A, B and E might belong to a triplet-triplet transition, with intervals of 390 and 562 cm^{-1} . After the identification of two more systems C and D, Krishnamurty considers that systems E, D and C with separations of 55 and 110 cm^{-1} may better be represented as belonging to an electronic triplet, while A and B may be identified as two component systems of a triplet \rightarrow triplet transition. According to us, each of the brief systems A to I consisting of single headed bands arises from a transition with $\Delta\Lambda = 0$ in Hund's case (a). However in view of the large multiplet splittings known in the ground and low excited states of CoI , it is possible that they are all separate systems with $\Delta\Omega = 0$ corresponding to Hund's case (c). This view is supported by the fact that Heimer, (1937) from a detailed rotational analysis of CoH bands, has previously identified the $A \rightarrow X$ transition in CoH as $\Omega = 4 \rightarrow \Omega = 4$ with $\Delta\Omega = 0$, corresponding to Hund's case (c).

The characteristic appearance of the N_1 and N_2 systems observed in the photographic infrared region ($\lambda 6850 - \lambda 7200 \text{ \AA}$) shown in strip (d) in Plate XII B, Fig. 2, would suggest that they may arise from two components of a $^3\Pi - ^3\Sigma$ transition. The magnitude of the vibrational constants of the upper and lower states, the observed double headed nature of the bands, and the close proximity of these two systems lend support to this view. However, both the upper and lower states of this $^3\Pi - ^3\Sigma$ transition do not correspond to those observed already in the visible region. They appear to belong to two different excited states of the CoCl molecule. A similar situation is also observed in the band systems of MnF, MnCl and MnBr in the photographic infrared.

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ROLE PLAYED BY AMMONIUM SALTS IN THE CLEARING OF NUCLEAR EMULSIONS

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ABSTRACT. The effect of the addition of various ammonium salts (ammonium chloride, ammonium sulphate, and ammonium acetate) to the usual hypo solution on the clearing time of nuclear emulsions and also their influence on the grain size and the shrinkage factor, have been investigated in view of some contradictory results reported by various authors in recent years. The addition of the ammonium salts has been found to cause a decrease in the clearing time, and then a slight increase after attainment of the optimum concentration. The addition of ammonium salts, however, has been found to have no effect on the grain size or the shrinkage factor of nuclear emulsions. Results obtained have also been explained on the basis of the current theory.

Thick emulsions necessitate longer clearing times, and this prolonged fixation leads to severe distortions in nuclear emulsions. As such, the methods for decreasing the clearing time have been studied by various authors, and it has been found that the addition of ammonium salts to hypo decreases the fixation time considerably, because the ammonium salts of hypo are better complex forming salts with silver halides than the sodium salts of hypo.



Piper worked on this problem, and investigated the change in the clearing time of thin plates with a change in the concentration of ammonium salts. He reported a fall in the clearing time with an increase in the concentration of the ammonium salt, till an optimum concentration is attained, after which, the clearing time has been reported to increase again. Also, according to him the $\langle\langle\text{Cl}\rangle\rangle$ ion in ammonium chloride is responsible for eating up the developed grains, near the surface of the emulsion.

Prakash *et al.* (1958) reported a contradiction to the observations made by Piper. According to them, the clearing time decreases up to an optimum concentration of the ammonium salt, after which it remains more or less constant, and does not have an appreciable rise as reported by Piper.

In view of the above contradictions the author found it useful to take up some work in this direction. The observations and the results thus arrived at are reported in this paper.

EXPERIMENTAL PROCEDURE

The ammonium salts selected were ammonium chloride, ammonium acetate and ammonium sulphate. The first salt was selected, because in addition to ammonium thiosulphate the chlorine ion concentration affects the diffusion rate of the fixer, and therefore, may suppress the reaction and also because it offers a direct verification of the observations made by Piper and those due to Prakash *et al.* Ammonium sulphate and acetate were selected so as to study the effect due of any other two suitable ammonium salts, not tried so far.

For this work Ilford K_2 plates of 100, 200, and 400 microns, and also K_0 and G_5 plates of 200 micron thickness were used, so as to study the effect on the clearing time by a change in the thickness and type of the emulsion. Further, the experiments were conducted in the following stages :

1) Effect of the change in the concentration of ammonium chloride on the clearing time of K_2 Ilford 100 micron plates K_2 and G_5 was studied, using different concentrations of hypo. Plates were directly put in the fixing solution maintained at 17°C . Care was taken to see that the level of the fixing solution is same in all the three cases. The results are plotted as shown in Fig. 1.

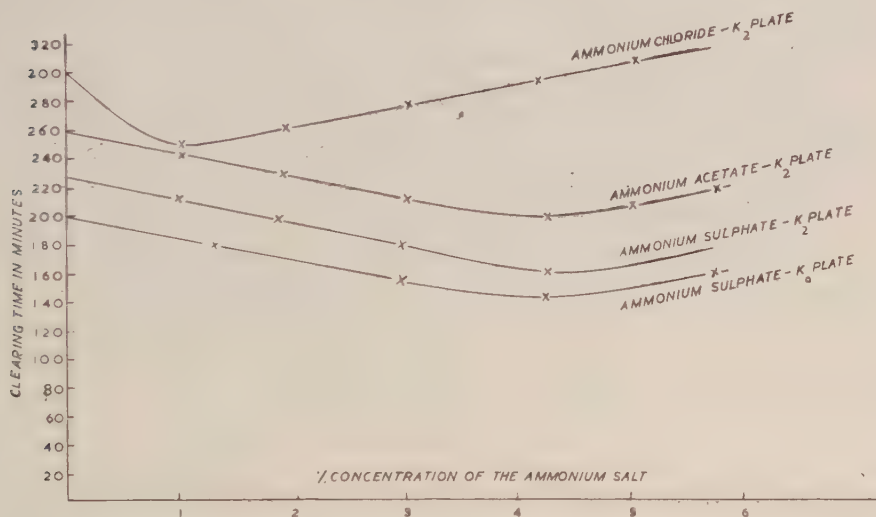


Fig. 1. The percentage concentration of NH_4Cl against the clearing time in minutes for different concentrations of hypo for 100 plates K_2 & G_5 (temperature 17°C).

The curves show a fall upto an optimum value of concentration, and then a rise, although the rise is not as pronounced as reported by Piper. Moreover, a shift in the position of optimum concentration was observed with a change in the hypo concentration, as shown in Fig. 1. Change in the type of emulsion, however, has been found to have no effect on the clearing time of the emulsion.

2) Secondly, the change in the clearing time of K_2 and K_0 200 micron plates with a change in the concentration of the three ammonium salts was studied. A

fall, and then a rise has been observed in the case of all the three curves, for ammonium chloride, ammonium sulphate and ammonium acetate. The rise is more pronounced in the case of ammonium chloride than in the case of other two ammonium salts. Results, which have further been found to be independent of the type of emulsion used, are represented in Fig. 2.

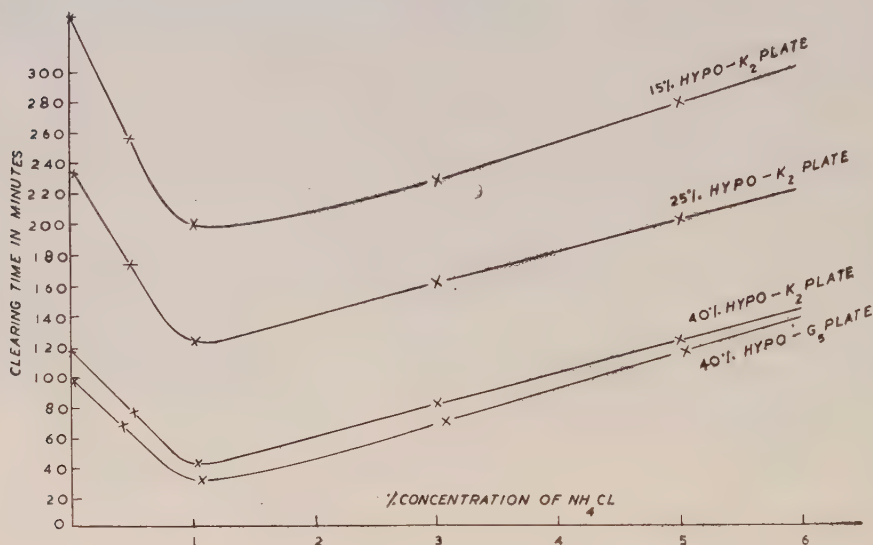


Fig. 2. Percentage concentration of various ammonium salts clearing time in minutes for 200 Ilford K₂ & K₀ plates temperature during clearing 17°C hypo concentration in each solution 40%

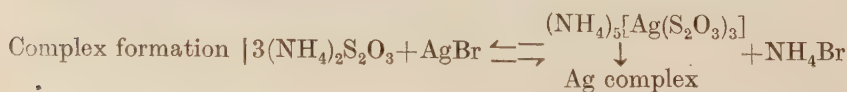
3) Thirdly, the effect of the emulsion thickness over the percentage reduction in the clearing time was investigated in the case of K₂ plates for all the three ammonium salts. The curves were found to have a fall up to 200 microns in all the cases excepting for ammonium chloride where the fall persists beyond 200 microns. These results are plotted as shown in Fig. 3.

RESULTS AND DISCUSSION

The results may be discussed in light of the three stages of observations mentioned above.

1. The rise and fall of curves shown in Fig. 1 can be accounted for as follows :

Ammonium salts of hypo being better complex forming salts with silver halides, as compared to sodium salts of hypo, any increase in the concentration of the ammonium salts should decrease the clearing time.



The optimum concentration can be explained on the basis of the reversible nature of the reaction, and so also the shift in the position of the optimum with respect to different hypo concentrations. The rise in the curves may be explained as being due to the fact that higher complexes of ammonium thiosulphate and silver halides are unstable as compared to the higher complexes of sodium thiosulphate, and silver halides. The clearing time, however, is independent of the type of the emulsion as is expected.

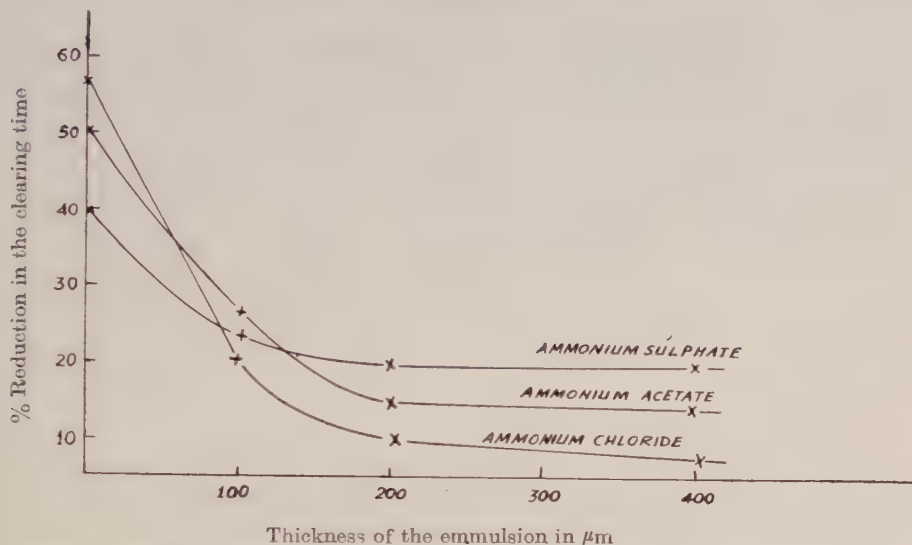


Fig. 3. Emulsion thickness Vs % reduction in the clearing time.

2) A fall, and then a rise in the curves is obtained in case of all the three ammonical salts, as is explained on the basis of the explanations given above. The more pronounced rise observed in the case of ammonium chloride can be explained as being due to the presence of $\ll \text{Cl} \gg$ ion which effects the rate of diffusion, as chlorine harden the gelatine of the emulsion, thereby increasing the clearing time by effecting the diffusion rate. As this factor is absent in the case of other two ammonium salts, the rise is not as pronounced in their case,

3) The percentage fall goes on decreasing in the case of higher thicknesses for NH_4Cl , whereas for other salts it remains constant after 200 microns. The reason for this is that upto 200 microns the diffusion velocity of the fixing solution decreases with an increase in the thickness, and hence a fall in the curve. In case of ammonium chloride this effect persists beyond 200 microns, because of the contribution of the $\ll \text{Cl} \gg$ ion, which, however, is not the case with other ammonium salts. Also, the diffusion velocity becomes independent of emulsion thickness beyond $200\mu\text{m}$, which explains the flatness of the curves beyond $200\mu\text{m}$.

Effect on the shrinkage factor and the grain size:

Effect on the grain size was investigated so as to find out whether or not the chlorine eats away the developed grains at the surface as reported by Piper.

For this, the grain size at the top and the bottom of the plate was found in case of pure hypo, and hypo with each of the other ammonium salts. (The optimum concentration being used in each case). The plates of the same type were simultaneously put in the four different baths and the fixing carried out under the same experimental conditions. The observations regarding the shrinkage factor and the grain size are shown in Tables I and II

TABLE I
Observations regarding the shrinkage factor

Plate thickness in μm	Shrinkage factor			
	Pure hypo	Hypo with optimum concentration of NH_4Cl	$(\text{NH}_4)_2\text{SO}_4$	$\text{NH}_4\text{C}_2\text{O}_4\cdot\text{H}_3$
100	2.00	2.16	2.05	2.04
200	2.50	2.60	2.4	2.72
400	2.75	2.50	2.50	2.75

TABLE II
Observations regarding the grain size

Thickness of the plate in μm	Surface of emulsion	Grain size			
		Free hypo	Hypo having optimum concentration of NH_4Cl	$(\text{NH}_4)_2\text{SO}_4$	$\text{NH}_4\text{C}_2\text{O}_4\cdot\text{H}_3$
100	Bottom	0.5	0.75	0.5	0.5
	Top	0.5	0.50	0.5	0.5
200	Bottom	0.75	0.75	0.5	0.75
	Top	0.75	0.75	0.75	0.75
400	Bottom	0.5	0.75	0.5	0.50
	Top	0.75	0.75	0.75	0.50

The study of the shrinkage factor, and the grain size reveals that within the allowed statistics, the shrinkage and the grain size is in no way affected by the addition of the ammonium salts. It also contradicts the hypothesis that chlorine is responsible for eating away the emulsion at the surface. The optimum concentration of the various ammonium salts used by the author are 1.5% for ammonium chloride, 2.5% for ammonium sulphate and 2.5% for ammonium acetate. Relative study of the suitability of these salts as regards the clearing of thick plates :

For thick plates the clearing time depends predominantly upon the diffusion velocity of the fixing solution, as against the thin plates. Consequently then

pH value of the fixing solution becomes an important factor. To make a relative study of the usefulness of these salts as regards the clearing of thick plates, pH values of the various concentrations of these solutions were calculated by the usual formulae, Vogel (1958). The results are shown in Table III:

TABLE III
Observations regarding clearing time

Conc. of the amm. salt %	.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
pH-of $(\text{NH}_4)_2 \text{SO}_4$ - (optm. conc.) + hypo (40%)	5.3	5.6	5.8	6.2	5.7	5.6	5.3	5.0
pH of $\text{NH}_4 \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ - (optm. conc.) + hypo (40%)	6.3	6.8	6.9	6.0	7.4	7.8	7.9	8.1
pH-of $\text{NH}_4 \text{Cl}$ (optm. conc.) + hypo (40%)	6.1	6.5	6.7	6.8	6.2	5.7	5.4	5.2

The table clearly shows that the pH value of hypo+amm. sulphate and also hypo+amm. chloride solution is well within the acid region, thus ensuring a high diffusion velocity, and the pH value of amm. acetate being in the basic region, it does not have a high diffusion velocity. Therefore, amm. acetate+hypo is not as suitable for clearing as the other two salts. Amm. sulphate, however, has been found to be most suitable for this purpose.

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DIRECTIONAL PROPERTIES OF EXTENSIVE AIR SHOWER ARRAYS

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ABSTRACT. The simple extensive air shower array proposed by Shen and Singer (1957) for which they claimed about 90% directional efficiency, has been tested by two groups of physicists, McCusker *et al.* (1959) and Layson *et al.* (1960), using it in conjunction with cloud chambers and scintillation counters, respectively. They concluded that the proposed set up has got very poor efficiency in selecting showers in preferred directions. It is pointed out that there are some significant differences between the results of various authors, on this problem and that it is possible to make further improvements in the performance of the device, besides the two methods suggested by McCusker *et al.* (1959).

INTRODUCTION

Shen and Singer (1957) proposed a simple extensive air shower array consisting of three G. M. counter telescopes, placed at the vertices of a triangle, for which they claimed a directional efficiency of 90%. This arrangement has been tested by McCusker *et al.*, (1959) using a similar unit in conjunction with two cloud chambers. From their experimental results they concluded that there is no great improvement in the angular resolution of the apparatus suggested by Shen and Singer, and it is not of much value in looking for anisotropy in the high energy primary cosmic radiation. Their results indicate that the vertical arrangement leads only to 7% (or at the best 14%) enrichment of showers coming from the near vertical direction. But our results (Bhaskara Rao and Gill, 1960), obtained during the course of an investigation on the influence of geomagnetic field on extensive air showers at Gulmarg, suggest an enrichment value of the order of 55%. With a view to check our Gulmarg data, a similar experiment has been conducted at Aligarh (alt. 680 ft.), again with two telescopes. The experimental results give an enrichment figure of 54% which is very high when compared to that of McCusker *et al.* Moreover, McCusker *et al.*, contented that there is no serious disagreement between their own results and those of Shen and Singer. Even this contention is not justifiable as shown at a latter stage. Further, their results are in disagreement not only with our results, but also with those of Shen and Singer and of Rathgeber (1959). Although the experimental results of Layson *et al.* (1960) agree well with their theoretical calculations, their shower data do not seem to follow the well established $\cos^n \theta$ law. Finally, whatever might be the actual directional efficiency and usefulness of the shower array proposed by Shen

and Singer, the observed discrepancies are very significant and worth consideration. Further slight improvements can be made in the device.

EXPERIMENTAL

The arrangement used consisted of two G.M. counter telescopes of semiangle 10° , with two trays in each. Each tray consisted of four counters connected in parallel. The telescopes could be tilted independently around any axis. All other details of the experiment were exactly the same as mentioned in our paper (Bhaskara Rao and Gill, 1960).

The separation between the telescopes was 40m. Fourfold coincidences were recorded in the East-West and North-South planes, the telescopes being fixed in three positions, vertical, 45° zenith angle and horizontal, in rotation. The position of the telescopes was changed from the E-W plane to N-S plane and vice versa for every twenty days. The data were corrected for pressure and temperature variations using $\beta = -10\% \text{ cm}^{-1}\text{Hg.}$, and $\theta_r = -0.38\% \text{ per degree C.}$, respectively. Then the average of the shower rates in the two planes was calculated.

RESULTS AND DISCUSSION

Here four instances are given, including our own results at Aligarh, to point out the large discrepancies between the results of various authors.

(A) The shower rates corresponding to 40 m separation of the telescopes were given in Table I.

TABLE I
Coincidence rate vs. zenith angle

Zenith angle 'Z'	Average coincidence rate per hour
0°	4.98 ± 0.08
45°	3.69 ± 0.07
90°	2.30 ± 0.06

$$\text{Percentage enrichment} = \frac{V-H}{V} \times 100\% = 54\%$$

Where V = Coincidence rate with telescopes in the vertical position,
 H = Coincidence rate in the horizontal position.

Here it should be remembered that the experimental results of McCusker *et al.*, actually give only 7% enrichment which is very low when compared to our value of 54% .

(B) Some of the experimental results of Rathgeber.

TABLE II
Shower rate in counts per hour

Zenith angle 'Z'	Counters in each telescope.	
	(X) 2 counters	(Y) 3 counters
0°	1.96 ± 0.29	1.56 ± 0.27
90°	1.25 ± 0.23	0.77 ± 0.16

From the columns (X) and (Y), enrichment values can be calculated as 36% and 51% respectively. Evidently, there is large difference between the enrichment values of McCusker *et al.*, and Rathgeber.

(C) Comparison of the experimental results of Shen and Singer and McCusker *et al.*

TABLE III
Experimental determination of zenith angle distribution

Separation between the extreme counters in cms.	Effective zenith angle	Difference of effective zenith angle	Six fold coincidence rate per hour	Percentage difference in the coincidence rate.
Shen and Singer				
(i) 46.2	6.3°	13.2°	0.30±0.020	55%
(ii) 14.8	19.5°		0.46±0.025	
McCusker <i>et al.</i> ,				
(i) 67.0	5.6°		0.605±0.039	14%
(ii) 15.0	24.8°	19.2°	0.692±0.029	

The experimental set up used by McCusker *et al.*, was just similar to that of Shen and Singer. Shen and Singers' results show a difference of 55% in the counting rate for a difference of 13.2° in the effective zenith angle, whereas those of McCusker *et al.*, show only a variation of 14% for 19.2° difference of effective zenith angle. In fact McCusker *et al.*, should have observed a difference larger than 55%. Moreover, McCusker *et al.*, contented that their experimental results are not in serious disagreement with those reported by Shen and Singer. From the above table it is easy to see how they are not justified in their contention.

(D) Experimental results of Layson *et al.*, (1960) :

The directional response of the same set up was also tested by Layson *et al.*, using it in conjunction with the Sydney air shower apparatus. Although they claim that their experimental results are in good agreement with their theoretical calculations, their data do not seem to follow the well known $\cos^2\theta$ law. The zenithal distribution of showers given by them in the form of histogram, (corres-

ponding to all showers) is compared with the distribution obtained by McCusker *et al.*, with the help of cloud chambers. Even if the directional efficiency of the system were to be low the observed data should have followed the $\cos^2\theta$ law. Data obtained by McCusker, *et al.*, follows the theoretical distribution well, but the histogram given by Layson *et al.* is much different from what it ought to be. From Fig. 1(b) it can be seen that the telescopic system records more showers at larger zenith angles (from 5° – 40° , at an interval of 5°) than from the vertical and near vertical i.e., 0° – 5° . In particular the shower rate at 20° – 25° is four times the rate at 0° – 5° . This discrepancy is of very serious nature, which requires

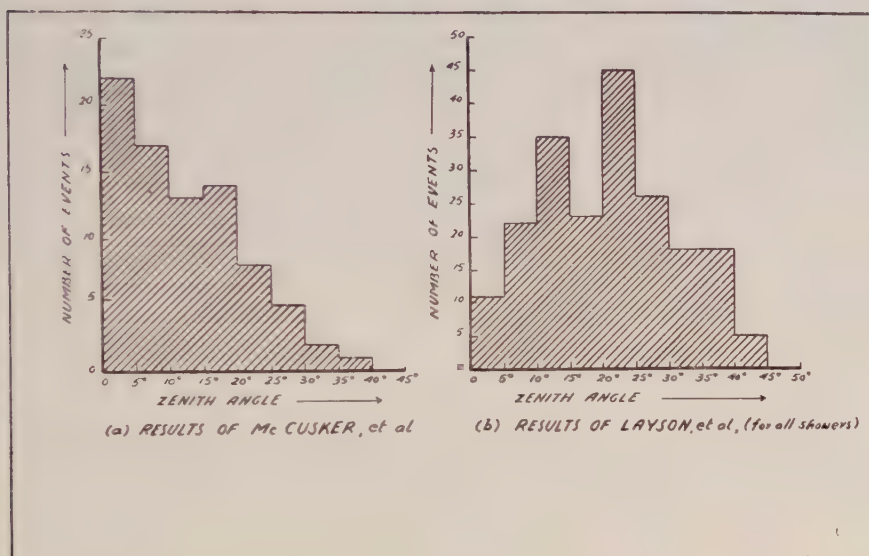


Fig. 1. The frequency of showers of different zenith angles setting off the arrangement.

some explanation. Rossi (1960) attributed the flat distribution of showers observed at Alto (alt. 4100m; shower size $10^7 < N < 3 \times 10^7$) to the fact that the showers are still near their maximum development. But the same arguments cannot hold good in the case of showers recorded at Sydney.

In view of the significant discrepancies in the experimental results of McCusker *et al.*, and other workers, and the irregularities of basic value in the zenithal distribution of showers recorded by Layson *et al.*, one should be cautious in drawing a quantitative conclusion regarding the directional efficiency of the shower array. It is to be emphasized that the directional efficiency of an array decreases at larger zenith angles because of the nonuniformity of the side shower background. McCusker *et al.*, suggested two ways to improve the performance of the device. This can be still improved by using sets of two or more counters connected in parallel, in the telescopes, instead of single counters, at the same time keeping the aperture of the telescopes constant by adjusting the separation between the upper and lower sets suitably. This offers larger sensitive area for shower particles

coming within the defined aperture of the telescopes and helps in reducing the percentage background of side showers from zenith angles, other than the defined aperture, in which we are not interested. This background can also be reduced by increasing the multiplicity of coincidence from six to nine, with a third set of counters in between the upper and lower sets of each telescope. These modifications do not have any significant effect on shower particles falling within the defined angle, but considerably reduce the background.

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UNLIKE MOLECULAR INTERACTIONS FOR $\text{CO}_2\text{--N}_2$ AND A FEW OTHER GAS MIXTURES

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ABSTRACT. A study of unlike molecular interaction for gas mixtures composed of several slightly non-spherical molecules and also for mixtures having non-spherical and spherical molecules has been done from the observed temperature dependence of second virial coefficient and thermal diffusion factor, assuming a Lennard-Jones (12 : 6) potential energy function. It has been found that this potential energy function which is strictly applicable to spherical molecules can be applied with success to discuss properties of gas mixtures composed of molecules which deviate slightly from spherical symmetry. Further, the values of the potential parameters indicate the inadequacy of simple combining rules for the case of gas mixtures considered here.

INTRODUCTION

The influence of the law of molecular interaction on properties of gases and gas mixtures is well known and in principle, information about the potential parameters for like and unlike interactions should be obtainable from the experimental determinations of various bulk properties as a function of temperature. Unfortunately, the experimental data for gas mixtures which might lead to a knowledge about the forces between unlike molecules are very meagre. In many cases, the measurements are confined to a single temperature and hence are unsuitable for obtaining any reliable information about intermolecular forces. Thus, generally, for a proper understanding and evaluation of these forces between unlike molecules, use is made of certain empirical combining rules, involving the force parameters of pure components, which have no theoretical justification. Further, these simple combining rules may be valid for central force fields but are certainly not appropriate when we wish to treat molecules like CO_2 . Thus, it is very useful and desirable to study the unlike molecular interactions from the temperature variation of properties of gas mixtures wherever such data are available.

For discussing and correlating the different properties of gases and gas mixtures, various formulated expressions for the potential energy function are utilized, such as the Lennard-Jones (12:6) and the modified Buckingham (Exp:6) functions. The (Exp:6) function is said to be more realistic and more flexible, but both of

them had practically the same success in predicting the properties of gases and it is difficult to establish the superiority of one potential over the other as has been concluded by Madan (1955), Mason and Rice (1954) and DeRocco and Halford (1958). However, the (12:6) potential energy function is definitely much simpler and easy to handle and has, therefore, been widely used.

Srivastava and Madan (1953) utilized the temperature variation of thermal diffusion factor for the study of the law of molecular interaction for some gas pairs on the (12:6) model. Later, Srivastava and Srivastava (1957, 1959) and Srivastava (1957) used the properties of interdiffusion and thermal diffusion, mostly of rare gas mixtures, for this purpose on the (Exp:6) model. The assumptions in the theory make both the potential energy functions strictly applicable to spherically symmetric molecules, such as those of monatomic gases at moderate pressures. When the molecules of a gas are not spherically symmetric, there are great mathematical difficulties in discussing their properties rigorously and there is no completely adequate analysis of intermolecular forces between asymmetric polyatomic molecules. However, the theory based on the above mentioned potential energy functions has had success in correlating transport phenomena in polyatomic gases and the assumptions may not be a severe limitation as has been discussed by Chapman and Cowling (1952). It is also seen that rather high asymmetry is required before deviations from the force law applicable to spherical molecules become appreciable. Thus, the same law can be taken to describe the properties of molecules which are slightly non-spherical and for all practical purposes, such derivations will be quite adequate. Further, they will also provide a means of extrapolation and interpolation of the existing data into regions of higher or lower temperatures.

In the present paper, we have used the (12:6) model to study the law of molecular interaction involving unlike molecules and have chosen two sets of binary gas mixtures. The one consisting of mixtures of diatomic gases with a common polyatomic gas such as mixtures of N_2 , O_2 and CO with CO_2 of H_2 with BF_3 and the other consisting of a monatomic gas with diatomic gases and also with a polyatomic gas such as mixtures of A with N_2 , O_2 and CO_2 and of Kr with N_2 . The latter set is interesting since it involves an interaction between spherical and non-spherical molecules.

Recently, Cottrell *et al.* (1956) determined the second virial coefficients of the mixtures of CO_2 with N_2 , O_2 , CO and A . Grew *et al.* (1954) have reported the experimental data on thermal diffusion of CO_2 - N_2 , A - N_2 , Kr - N_2 and A - O_2 and several other gas mixtures while Raw and Kyle (1956) have reported data on H_2 - BF_3 mixtures. We have utilized here both these sets of data for determining the potential parameters. For the gas mixtures chosen, there have been practically no attempts to estimate the potential parameters, in particular, using second virial coefficient and thermal diffusion factor and to correlate the experi-

mental data with the theory based on the Lennard-Jones (12:6) potential. The thermal diffusion of A--N_2 mixture has, however, been used by Srivastava and Srivastava (1957) for an (Exp:6) model and the diffusion data of $\text{CO}_2\text{--N}_2$ and $\text{CO}_2\text{--O}_2$ mixtures by Walker and Westenberg (1958, 1960) for a (12:6) and an (Exp: 6) model but an equilibrium property like the second virial coefficient has not been previously used for this purpose. Although the observed data for second virial coefficient are not too extensive in view of the experimental difficulties and limitations of measurement and also as this is the only data available for gas mixtures at more than one temperature (the other measurements are mostly at a single temperature and hence cannot be used in finding the parameters) it is considered worthwhile to examine these data and make the best possible use of them.

THEORY AND FORMULAE

The second virial coefficient B_M , for a gas mixture is given by the relation

$$B_M = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \quad \dots (1)$$

where x_1 , x_2 , B_{11} , B_{22} are the mole fractions and second virial coefficients of components 1 and 2 and B_{12} is the interaction second virial coefficient having a direct relation to the law of unlike molecular interaction through the reduced second virial coefficient B^* given by Hirschfelder, Curtiss and Bird (1954)

$$\left. \begin{array}{l} \text{as} \\ \text{where} \end{array} \right\} \begin{array}{l} B_{12} = b_{12} B_{12}^*(T^*) \\ b_{12} = \frac{2\pi}{3} N r_{12}^3 \text{ and } T^* = KT/\epsilon_{12} \end{array} \quad \dots (2)$$

The parameters ϵ_{12} and r_{12} are the depth of the potential well and the separation distance for zero potential energy for unlike molecular interaction.

The general expression for thermal diffusion factor is quite complicated and moreover, different theoretical expressions are available for this quantity such as those of Chapman and of Kihara. Kihara's expressions are much simpler than the corresponding ones of Chapman and are more accurate as has been observed by Srivastava (1957) and many others and have therefore been used here. $[\alpha_T]_1$, Kihara's first approximation formula for thermal diffusion factor may be written in the convenient form

$$[\alpha_T]_1 = (6C^* - 5)g \quad \dots (3)$$

where g is a complicated expression involving molecular weights, composition and collision integrals for which reference can be made to Srivastava (1957).

The principal contribution towards temperature dependence of thermal diffusion factor comes through the factor $(6C^* - 5)$ which involves only unlike interactions. The factor g depends only slightly on temperature. This slight

variation hardly shows any definite trend and is itself liable to uncertainties on account of various errors as has been observed by Srivastava and Madan (1953). Further, even if this variation is considered and is taken account of, as has been done by Srivastava and Srivastava (1957) and Srivastava (1957), the results do not show any appreciable variation, the deviations being well within the limits which result from considerations of the effect of the error in the experimental measurements. Thus $[\alpha_T]_1$ varying as $(6C^*-5)$ is quite reasonable for all paractical purposes.

DETERMINATION OF POTENTIAL PARAMETERS

The methods of determining the potential parameters from the experimental data have been discussed recently by Srivastava and Srivastava (1959), Whalley and Schneider (1955) and Strehlow (1953) and others. They mainly consist of (1) graphical ratio method used successfully by Srivastava and Madan (1953), Madan (1955), (1957), Sharma and Madan (1960) and Bunde (1955); (2) the translational method of Keesom (1912) and Lennard-Jones (1924); (3) the intersection method of Buckingham (1938). The translational method requires data over a large temperature range and unless there are some distinguishable peculiarities in the curve as has been discussed by Srivastava and Srivastava (1957), a multitude of translations is possible and the method fails. The intersection method requires accurate data for only a few temperatures which need not extend over a large temperature interval but the data must be highly accurate, otherwise it is impossible to determine the intersection point. Thus, for most cases, the first method, that is, the graphical ratio method, is quite adequate and suitable for examining and reducing the experimental data appropriately and deducing the potential parameters therefrom. The method is described in detail by Srivastava and Madan (1953), Sharma and Madan (1960) and Madan (1955) and a reference to these can be made.

Usually experimental B_{12} is obtained from B_M by using the calculated values of B_{11} and B_{22} utilizing the values of the force parameters obtained from other measurements which is not a very desirable procedure. To determine the parameters between unlike molecules, we have resorted to purely experimental data, that is, to get B_{12} (experimental), experimentally observed values of B_{11} and B_{22} have been utilized. The values of ϵ_{12}/k and r_{12} determined from the temperature dependence of second virial coefficient are reported in Table I, together with the temperature ranges for which they have been calculated. The potential parameters obtained from temperature dependence of thermal diffusion factor are given in Table II(a) & II(b). Using ϵ_{12}/k , the value of r_{12} has been calculated from experimental interdiffusion coefficient wherever such data are available. The potential parameters thus obtained from second virial coefficient and thermal diffusion factor are compared with other determinations including those obtained with the help of the combining rule viz., $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$ and $r_{12} = \frac{1}{2}(r_{11} + r_{22})$.

where ϵ_{11} , ϵ_{22} and r_{11} , r_{22} are respectively the depths of the potential wells and the separation distances for zero potential for (1:1) and (2:2) like interactions. These are reported in Tables III and IV.

DISCUSSION OF RESULTS

It will be quite interesting to see how far the potential parameters, obtained by us, agree with those derived from other sources and how satisfactorily these parameters can predict another bulk property. The comparison of parameters has been done in Table III and IV from which it can be seen that the parameters obtained by us are different from those derived using combining rules. The values of $\epsilon_{12}k$ are higher and those of r_{12} are lower than the corresponding combining rule values except for Kr--N_2 . A similar trend was noticed by Barua (1959). This is to be expected as the combining rule for r_{12} is true only for molecules which behave as rigid spheres.

The system $\text{CO}_2\text{--N}_2$ is interesting because parameters for this could be determined from both second virial coefficient and the thermal diffusion. The combining rule gives a value 134 for $\epsilon_{12}k$ whereas the second virial coefficient gives an indication that this value is $>>134$ and is about 168. This indication is further confirmed by evaluation of parameters from thermal diffusion factor, which is a more sensitive property and the value obtained is 157.1. This is in agreement with the value obtained by Walker and Westenberg (1958) from the temperature dependence of mutual diffusion. The parameters obtained from equilibrium and non-equilibrium properties are also seen to be different as has also been noticed in general by Hirschfelder *et al.* (1954) and Madan (1955, 1957).

Using the different parameters, we could, for comparison, compute the values of coefficient of interdiffusion, another property for which some data are available for these mixtures. This has been done in Table V. However, in general, the parameters derived from equilibrium properties should not be used for calculation of non-equilibrium properties or vice versa because different properties emphasize the potential energy curves differently and cannot be simply correlated. When we take two similar molecules, for example, two polyatomic molecules, we get a reasonably good agreement, but when we have a mixture of a polyatomic molecule with a simple molecule, the agreement is not satisfactory. The agreement between the theoretical and experimental values is good for $\text{CO}_2\text{--N}_2$ and $\text{CO}_2\text{--O}_2$ (rather it is better than that obtained by using parameters from combining rules) but not for $\text{CO}_2\text{--CO}$ and $\text{CO}_2\text{--A}$. In the latter case, for example of $\text{CO}_2\text{--A}$, the interaction is between a spherical and a non-spherical molecule. As expected (Srivastava and Srivastava 1959) due to the non-spherical nature of CO_2 molecule, the potential parameters calculated from second virial coefficient (equilibrium property) do not reproduce the coefficient of mutual diffusion (non-equilibrium property) satisfactorily. In this type of mixture, it seems that the effect of the non-spherical nature of the molecule predominates over that of the spherical

one, even though we can ascribe part of the discrepancy due to possible experimental errors in the measurement of the coefficient of mutual diffusion for this mixture for which there are the data of only one experimenter at a single temperature. This was obtained by Waldmann from a study of diffusion thermo-effect and is subject to much error as has been discussed by Chapman and Cowling (1952). Further, for this mixture, the thermal diffusion factor, a property very sensitive to the force law, increases with decrease of temperature, a peculiar yet unexplained behaviour, and it is not surprising that a good agreement is not obtained in this case.

The case of CO_2 -CO mixture is different. Here, the interaction is between a symmetrical molecule CO_2 with an asymmetrical molecule CO, unlike the interactions of CO_2 - N_2 or CO_2 - O_2 in which there are symmetrical molecules like N_2 or O_2 . Furthermore, the data on second virial coefficient for CO_2 -CO mixture shows practically no variation with temperature in the range 30°C to 60°C and an average curve had to be drawn for the determination of potential parameters which are subject to some uncertainty on this account.

In general, for all the gas mixtures, the non-spherical nature of the molecules does manifest itself and it is not surprising that a single set of parameters fails to give same degree of agreement for two different properties and also over a wide temperature range. For CO_2 - N_2 mixture, we find good agreement for the coefficient of mutual diffusion, but if the same parameters are used to compute the thermal conductivity, the agreement is not so good as has been reported by Brokaw (1959) and also computed by us and it necessitates the use of a different set of potential parameters for this purpose, even though the discrepancy may also be on account of the complex nature of the phenomenon of thermal conductivity for these molecules.

Unfortunately, for the gas pairs considered here, suitable and extensive data for different properties do not exist and as such, a detailed comparison with experiment is not possible. To arrive at any definite conclusions, it is very desirable to have more experimental data of various properties at different temperatures.

Nevertheless, the analysis is still useful and valid to a good approximation and is definitely of much interest in the absence of sufficient information about the forces between unlike molecules. The evaluation of the potential parameters from the experimental data for the study of forces between unlike slightly non-spherical molecules and the bulk properties of their mixtures, is definitely a better approach than the derivation of these parameters from simple combining rules which are semi-empirical in nature and may be valid only for central force fields.

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TABLE I
Values of potential parameters from second virial coefficient

Gas pair	CO_2-N_2		CO_2-A		CO_2-O_2		CO_2-CO	
Temperature range ($^{\circ}K$)	ε_{12}/k ($^{\circ}K$)	r_{12} (\AA)	ε_{12}/k ($^{\circ}K$)	r_{12} (\AA)	ε_{12}/k ($^{\circ}K$)	r_{12} (\AA)	ε_{12}/k ($^{\circ}K$)	r_{12} (\AA)
290-348	166.8	3.560	156.1	3.426	150.3	3.682	179.8	3.272
300-360	169.3	3.516	157.4	3.409	176.5	3.217	179.1	3.281
310-372	170.6	3.492	158.7	3.383	—	—	181.3	3.255
Mean	168.9	3.523	157.4	3.406	163.4	3.449	180.1	3.269

TABLE IIa
Values of potential parameters from thermal diffusion

Gas pair	CO_2-N_2	$A-N_2$	$A-O_2$	$Kr-N_2$
Temperature range ($^{\circ}K$)	$\varepsilon_{12}/k(^{\circ}K)$	$\varepsilon_{12}/k(^{\circ}K)$	$\varepsilon_{12}/k(^{\circ}K)$	$\varepsilon_{12}/k(^{\circ}K)$
125-250	—	—	—	113.8
150-300	—	112.0	121.9	114.5
175-350	—	111.5	115.1	109.4
200-400	—	109.9	119.0	104.2
225-450	—	108.7	122.9	103.7
250-500	170.0	104.2	126.9	105.5
275-550	164.7	—	—	110.5
300-600	154.6	—	—	111.1
325-650	147.7	—	—	115.3
350-700	142.3	—	—	116.0
Mean	157.1	109.2	121.2	110.7
$r_{12}(\text{\AA})$	3.557	3.428	3.309	—

TABLE IIb

H_2-BF_3		
Temperature range ($^{\circ}K$)	$\varepsilon_{12}/k(^{\circ}K)$	Mean $\varepsilon_{12}/k(^{\circ}K)$
340-408	104.3	
350-420	98.3	98.9
360-432	94.2	

TABLE III

Comparison of potential parameters obtained from second virial coefficient with those determined from other sources

Gas pair	$\varepsilon_{12}/k(^{\circ}K)$			$r_{12}(\text{\AA})$		
	(*)	(a)	(b)	(*)	(a)	(b)
CO ₂ —N ₂	168.9	132	134.1	3.523	3.839	4.095
CO ₂ —A	157.4	153	150.5	3.406	3.707	3.948
CO ₂ —O ₂	163.4	147	149.4	3.449	3.715	3.975
CO ₂ —CO	180.1	145	137.6	3.269	3.793	4.125

(*) Present work

(a) Combining rule, individual parameters from viscosity.
Hirschfelder, Curtiss and Bird (1954).

(b) Combining rule, individual parameters from second virial coefficient.
Cottrell *et al.* (1956)

TABLE IV

Comparison of potential parameters obtained from thermal diffusion with those determined from other sources.

Gas pair	$\varepsilon_{12}/k(^{\circ}K)$				$r_{12}(\text{\AA})$			
	(*)	(**)	(a)	(b)	(*)	(**)	(a)	(b)
CO ₂ -N ₂	157.1	168.9	157	132	3.557	3.523	3.516	3.839
A-N ₂	109.2	—	—	106	3.428	—	—	3.550
A-O ₂	121.2	—	—	118	3.309	—	—	3.426
Kr-N ₂	110.7	—	—	132	—	—	—	—
H ₂ -BF ₃	98.9	—	—	80.37	—	—	—	—

(*) From thermal diffusion (present work)

(**) From second virial coefficient (present work)

(a) Walker and Westenberg (1958)

(b) Hirschfelder, Curtiss and Bird (1954). Combining rule and individual parameters from viscosity.

TABLE V
Comparison of calculated and experimental values of interdiffusion

Gas mixture	Temperature (°K)	(*) D_{12} Cm ² /Sec	(a) D_{12} Cm ² /Sec.	experimental D_{12} cm ² /Sec.(b)
$\text{CO}_2\text{--N}_2$	273.2	0.141	0.130	0.144
	288.2	0.156	0.143	0.158
	293.2	0.161	0.147	0.160
	298.2	0.166	0.152	0.165(c)
				0.167(d) 0.168(e)
$\text{CO}_2\text{--A}$	293.2	0.159	0.136	0.140
$\text{CO}_2\text{--O}_2$	273.2	0.143	0.128	0.139
				0.137(f)
	293.2	0.163	0.146	0.160 0.153(f)
$\text{CO}_2\text{--CO}$	273.2	0.163	0.128	0.137

- (*) Present work, parameters are given in Table I.
 (a) Calculated using combining rules, individual parameters from viscosity.
 Hirschfelder, Curtiss and Bird (1954).
 (b) Data taken from Hirschfelder, Curtiss and Bird (1954) unless stated otherwise.
 (c) Boyd *et al.* (1951)
 (d) Walker and Westenburg (1958).
 (e) Boardman and Wild (1937)
 (f) Walker and Westenburg (1960)

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RAMAN AND INFRARED SPECTRA OF 1-FLUORO-2, 4-DINITROBENZENE AND 1-CHLORO-2, 4-DINITROBENZENE*

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Plate XIII

ABSTRACT. The Raman and infrared spectra of 1-fluoro-2,4-dinitrobenzene and 1-chloro-2,4-dinitrobenzene have been investigated and the observed frequencies have been assigned to different modes of vibration of the ring, by assuming C_2 symmetry for the molecules. Some of the vibrational frequencies due to vibrations within the NO_2 group have also been identified. It is observed that some of the modes of the skeleton C-C ring which are forbidden in infrared and *vice versa* in the case of benzene, appear in the spectra and it is concluded that the symmetry of the skeleton ring is disturbed by the substituents.

INTRODUCTION

The assignment of vibrational frequencies of some trisubstituted benzene compounds was made recently by Deb and Banerjee (1960) by studying the Raman and infrared spectra of the compounds. Such assignment was not made by any previous worker in the case of 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene. In fact, the infrared spectra of these two compounds and the Raman spectra of the fluoro compound were not known. The present investigation was undertaken to study the infrared spectra of these two compounds and the Raman spectrum of 1-fluoro-2, 4-dinitrobenzene and to identify the frequencies of different modes of vibration of the molecules. The fluorine and chlorine substituted compounds have been chosen, because by comparing the spectra it might be possible to get some results which would help accurate assignment of the frequencies.

EXPERIMENTAL

The compounds supplied by E. Merck were of guaranteed reagent quality. The liquid 1-fluoro-2, 4-dinitrobenzene was distilled under reduced pressure before use while the chloro compound was purified by crystallization from benzene. The infrared spectra were recorded with a Perkin Elmer Model 21 spectrophotometer with rocksalt optics, the resolution dial being set at 927. The absorption

*Communicated by Professor S. C. Sirkar

spectra of very thin films of the substances enclosed between NaCl plates were recorded. In the case of 1-chloro-2,4-dinitrobenzene the molten compound was poured on a hot NaCl plate and a similar hot plate was placed on it so that a thin film of the pure substance was enclosed between the plates. The spectrum of the solidified film was recorded. The Raman spectra of both the compounds were recorded on Ilford Zenith plates using a Fuess Glass Spectrograph of large dispersion. Iron arc spectrum was also photographed on the plate for

TABLE I
Raman and infrared frequencies of 1-fluoro-2,4-dinitrobenzene

Infrared bands ν in cm^{-1} & strength	Raman shift (cm^{-1}) & Intensity	Assignment
	164 (2b)	a'' fundamental
	300 (0)	a' "
	513 (1b)	a' "
630 (w)	634 (3)	
672 (w)		a'' "
706 (s)		a' "
743 (s)	742 (1b)	a'' "
813 (w)	811 (1)	a'' "
840 (vs)	835 (3)	a' "
917 (s)	925 (2)	a'' "
973 (wb)		
1008 (vw)		
1072 (s)	1070 (2)	a' "
1129 (ms)	1129 (1)	a' "
1153 (w)	1151 (5)	a' "
1244 (m)	1241 (2)	a' "
1272 (vs)	1269 (6)	a' "
	1296 (0)	
	1323 (2)	a' "
1347 (vs)	1346 (10)	a' "
1418 (ms)	1415 (3)	a' "
1490 (s)	1490 (2)	a' "
1525 (vs)		a' "
1551 (s)	1546 (6)	a' "
1606 (vs)	1616 (5)	a' "
1805 (w)		743 + 1072
1939 (w)		[706 + 1244 813 + 1129]
2082 (w)		917 + 1153 840 + 1244]
2877 (w)		1272 + 1606] 1347 + 1525]
2962 (w)		1551 + 1418
3100 (s)	3102 (2b)	a' fundamental

TABLE II
Raman and infrared frequencies of 1-chloro-2,4-dinitrobenzene

Infrared bands ν in cm^{-1} & strength	Raman shifts (cm^{-1}) & intensity (Harrand, 1953)	Assignment
	152 (1b)*	a'' fundamental
	205 (0)*	a' "
658 (w)	666 (1)	a'' "
687 (m)		a' "
730 (s)		a' "
745 (m)		a'' "
832 (ms)		a'' "
847 (m)	841 (1)	a' "
900 (s)		a'' "
912 (m)		
980 (vw)		
1040 (s)	1050 (1)	a' "
1080 (vwh)		
1099 (vw)	1109 (1)	a' "
1138 (m)		a' "
1151 (m)	1160 (2)	a' "
1210 (vw)		
1247 (w)	1255 (1)	a' "
1302 (wh)	1301 (2)	a' "
1346 (vs)	1358 (10)	a' "
	1396 (1)	
1421 (mh)		a' "
1459 (m)		a' "
	1472 (0)	
	1494 (0)	
1525 (vs)	1538.50 (1b)	a' "
1550 (s)		
1590 (vs)	1593 (3)	a' "
	1628 ?	
1698 (vw)		658 + 1040
1742 (vwh)		832 + 900
1785 (vw)		745 + 1040
1820 (vwh)		2 \times 900
1967 (w)		832 + 1138
2873 (wh)		1421 + 1459
3053 (w)		1459 + 1590
3100 (s)		a' fundamental

*Observed in the reinvestigated Raman spectrum by the present author.

comparison. The Hg line 4358 Å was first used to excite the Raman spectra but it was found that in the case of 1-chloro-2, 4-dinitrobenzene the absorption in the neighbourhood of the 4358 Å line was very strong and no line with Raman shift less than 666 cm^{-1} was observed. Hence the Hg line 5461 Å was used as the exciting line and Agfa Isopan plates were used to photograph the spectra.

RESULTS AND DISCUSSION

The spectrograms showing Raman lines of 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene are given in Figs. 1 and 2, Plate XIII and the infrared absorption curves are reproduced in Figs. 3(a) & (b) and 4(a) & (b). The

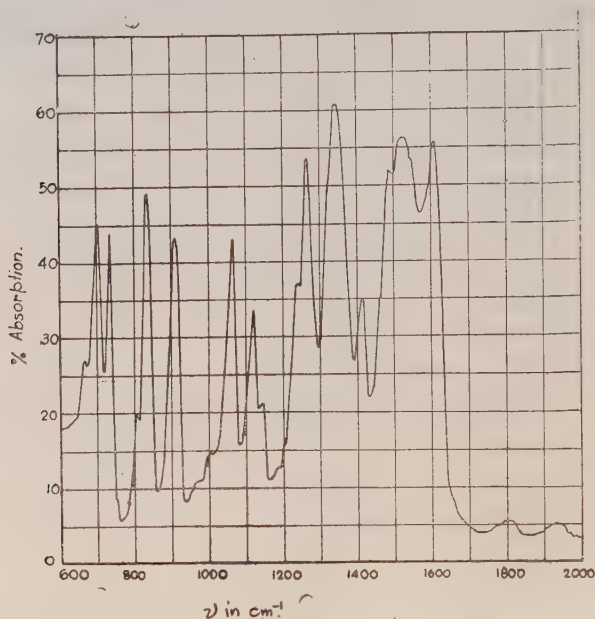


Fig. 3(a). Infrared spectrum of 1-fluoro-2,4 dinitrobenzene (liquid at 26°C)

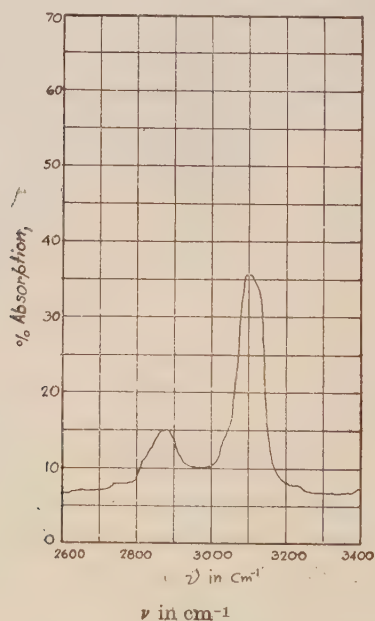


Fig. 3(b). Infrared spectrum of 1-fluoro-2,4 dinitrobenzene (liquid at 26°C)

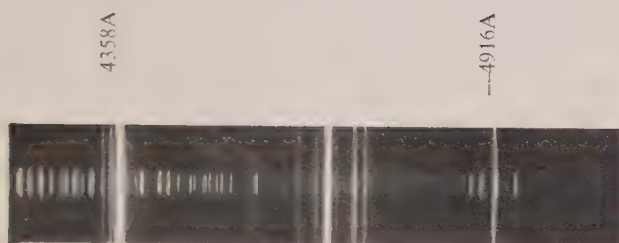


Fig. 1. Raman spectrum of 1-fluoro-2,4-dinitrobenzene (liquid at 30°C).

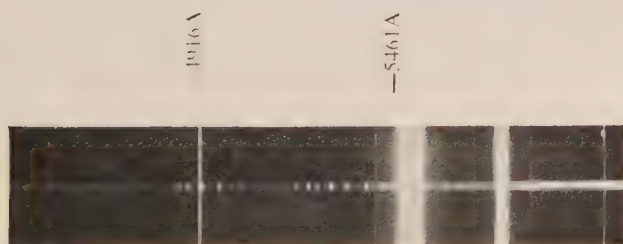


Fig. 2. Raman spectrum of 1-chloro-2,4-dinitrobenzene (solid at 30°C).



Raman shifts of the two substances and the infrared frequencies are given in Tables I and II respectively. The Raman frequencies of 1-chloro-2, 4-dinitrobenzene reported by Harrand (1953) have also been included in Table II. Tentative assignments of the lines are given in the third column of Tables I and II. The numbering of the modes of the vibrations has been made following that for the benzene ring made by Pitzer and Scott (1943).

The molecules of both the compounds belong to C_s point group, if the NO_2 group lies in the plane of the molecule. There are four modes of types a_{1g} , b_{1u} , e^+_{1g} and e^-_{1u} in the benzene molecule giving rise to a' type C—H valence oscillations in these two molecules. The infrared frequency 3100 cm^{-1} observed in the case of both the compounds represent such a' -type C—H vibrational frequency and they may be identified with e^-_{1u} mode in benzene (Mode No. 20) in which the two diametrically opposite C—H vibrate in opposite phases against the ring, the other substituents remaining almost stationary.

In the spectrum of 1-fluoro-2, 4-dinitrobenzene a characteristic frequency 1272 cm^{-1} is observed while in the spectrum of 1-chloro-2, 4-dinitrobenzene there is a characteristic frequency 730 cm^{-1} . These two frequencies approximate to C—F and C—Cl vibrational frequencies respectively and they are to be assigned to a' -type mode arising from e^-_{1u} type C—H stretching mode in benzene discussed above.

The degenerate e^-_{1g} mode of C—C vibration of frequency 1596 cm^{-1} (No. 8A, B) in benzene will split up into two components with reduction of symmetry to C_s , one of the components being slightly reduced in frequency and the other remaining almost unaffected. These two components have been identified with the strong infrared bands 1606 and 1551 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1590 and 1550 cm^{-1} of 1-chloro-2, 4-dinitrobenzene. The e^-_{1u} mode (No. 19A, B) in benzene similarly becomes a' -type vibration giving rise to the frequencies 1490 and 1418 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1459 and 1421 cm^{-1} of 1-chloro-2, 4-dinitrobenzene. These assignments are in agreement with those proposed for other 1, 2, 4-trisubstituted benzenes (Plyler *et al.*, 1957, Deb and Banerjee, 1960). These lines appear strongly in the Raman effect owing to the lack of centre of symmetry. The Raman frequency 513 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene might be a component of the e^+_{1g} vibration of benzene (No. 6A, B), which splits up into two frequencies with lowering of symmetry, the other component having a still lower frequency may be identified with the Raman line 300 cm^{-1} . This mode may give the Raman line 205 cm^{-1} in the 1-chloro compound, the other component being too weak to be recorded.

The a' -components of in-plane CH bending modes of the two molecules may be derived from similar modes a_{2g} (No. 3), b_{2u} (No. 15), e^+_{1g} (No. 9) and e^-_{1u} (No. 18) of benzene. Superposition of modes a_{2g} and e^+_{1g} of benzene may give rise to the mode of frequency 1244 cm^{-1} and 1247 cm^{-1} in the fluoro and chloro com-

pound respectively. Similar superposition of modes e^-_u and e^+_g may give rise to the frequencies 1153 and 1151 cm^{-1} in the two compounds. The frequencies 1129 and 1138 cm^{-1} of the two respective compounds may be similarly produced by the interaction of b_{2u} and e^-_u modes of benzene. The observed frequencies 706

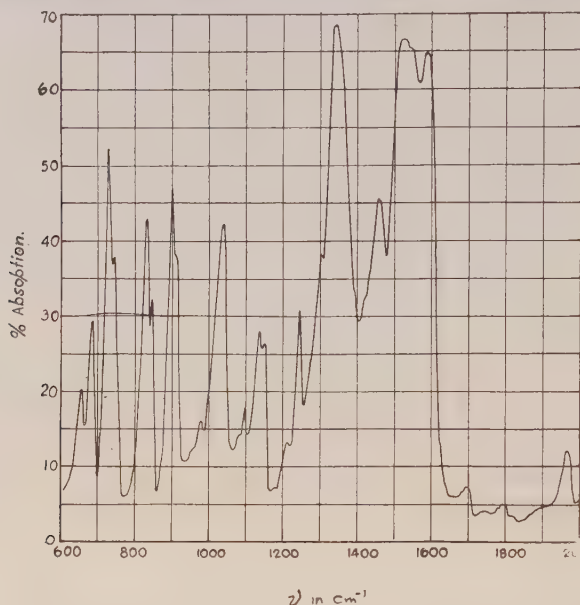


Fig. 4(a). Infrared spectrum of 1-chloro-2,4-dinitrobenzene (solid at 26°C).

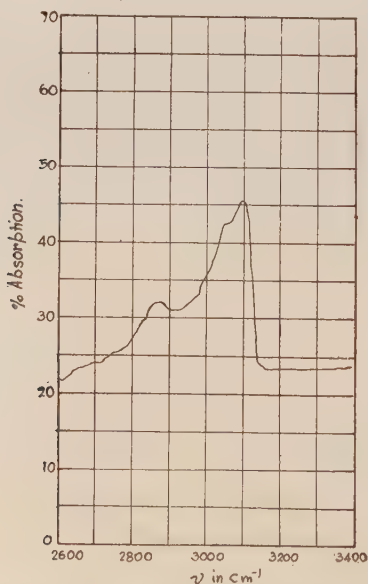


Fig. 4(b). Infrared spectrum of 1-chloro-2,4-dinitrobenzene (solid at 26°C).

and 1072 cm^{-1} in the case of the fluoro compound and 687 and 1040 cm^{-1} in the case of the chloro compound may represent components of the modes e^-_u and e^+_g .

The four out-of-plane CH bending modes of benzene (e^-_g , a_{2u} , e^+_u and b_{2g}) give such bending modes of type a'' in the case of these molecules assumed to belong to C_s point group. Superposition of modes b_{2g} (No. 5) and e^-_g (No. 10B) may give rise to a mode in which only the two diametrically opposite C—H bonds undergo out of plane bending. This frequency may be 917 cm^{-1} which appears both in Raman and infrared spectra of 1-fluoro-2, 4-dinitrobenzene (900 cm^{-1} in 1-chloro-2, 4-dinitrobenzene). The modes No. 10A and 17A of types e^-_g and e^-_u of benzene may similarly interact to produce frequencies 813 and 832 cm^{-1} observed in the spectra of the two compounds.

Norman Jones and Sandorfy (1956) discussed the occurrence of a C—H bending vibrational frequency at about 745 cm^{-1} in the case of 1, 2, 4-trisubstituted benzenes which is, according to them, known to be active only in Raman effect, but it should be noted that in the present work a strong frequency at 743 cm^{-1} in the case of 1-fluoro-2, 4-dinitrobenzene and a similar frequency at 745 cm^{-1} in the case of 1-chloro-2, 4-dinitrobenzene have been observed in the infrared. This can be obtained from superposition of the modes e^+_{1u} (No. 17A) and a_{2u} (No. 11).

The frequencies 672 and 658 cm^{-1} observed in 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene respectively represent out-of-plane carbon bending vibration corresponding to the b_{2g} mode in benzene (No. 4) which is expected to remain unaltered with substitution. The Raman frequency at 164 cm^{-1} observed in the case of the fluoro compound and 152 cm^{-1} in the case of the chloro compound may represent another such out-of-plane bending mode derived from e^+_{1u} mode in benzene (No. 16).

In the case of 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene, frequencies at 840 and 847 cm^{-1} respectively have been observed. Similar frequencies were also observed in the spectra of 2, 4- and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene (Deb and Banerjee, 1960). As suggested in a previous paper (Deb and Banerjee, 1960) these frequencies may originate from superposition of a_{1g} and b_{1u} modes (No. 1 and 12) in benzene. The frequencies 1323 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1302 cm^{-1} of 1-chloro-2, 4-dinitrobenzene may be a component of the e^+_g mode of benzene.

Besides these molecular frequencies, the spectra of both the compounds should contain frequencies due to vibration in the NO_2 groups. The results for fluoronitro- and chloronitrobenzenes obtained by previous workers have been tabulated in Landolt-Börnstein's Tables (1951). On comparing these results the frequencies 1525 and 1347 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1525 and 1346 cm^{-1} of 1-chloro-2, 4-dinitrobenzene can be readily identified with asymmetric and symmetric stretching vibration in NO_2 groups.

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I. for his kind interest and guidance and to Dr. S. B. Banerjee for valuable advice and help during the progress of the work.

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Letters to the Editor

The Board of Editors will not hold itself responsible for opinions expressed in the letters published in this section. The notes containing reports of new work communicated for this section should not contain many figures and should not exceed 500 words in length. The contributions must reach the Assistant Editor not later than the 15th of the second month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors.

6

PERIODICITY IN NUCLEAR BINDING ENERGY AND CORRELATION BETWEEN THE ISOTOPES OF DIFFERENT NUCLEI

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The binding energy of the nuclei is measured by the difference between the observed masses of the nuclei and the sum of the masses of the constituent nucleons. To explain the variation of the binding energy E for different nuclei, Bethe and Weiszäcker have proposed the following relation

$$E = -a_1 A + a_2 A^{2/3} + a_3 \frac{Z^2}{A^{1/3}} + a_4 \frac{(N-Z)^2}{4A}$$

where A is the atomic number, N and Z are the numbers of neutrons and protons and a_1 , a_2 , a_3 and a_4 are constants to be fixed by actual comparisons. The formula above, though broadly successful, is not adequate to explain precise mass data closely. Various efforts (Green, 1958 and Seeger, 1961) have been made to improve upon the Bethe-Weiszäcker relation by including pairing correction distinguishing nuclei composed of different combination of even and odd number of protons and neutrons, effects of shell structure and nuclear deformation and so on; however, the agreement of these improved formulae with observed data is not satisfactory. In view of this unsatisfactory situation, it is considered worthwhile to emphasize the deviations of the Bethe-Weiszäcker relation from the latest mass data of as many stable nuclei as are available and to see whether the deviations indicate any regular and systematic pattern.

Here we have plotted for different nuclei ΔM , the deviation of the experimentally observed binding energy (in MeV) from the Bethe-Weiszäcker relation

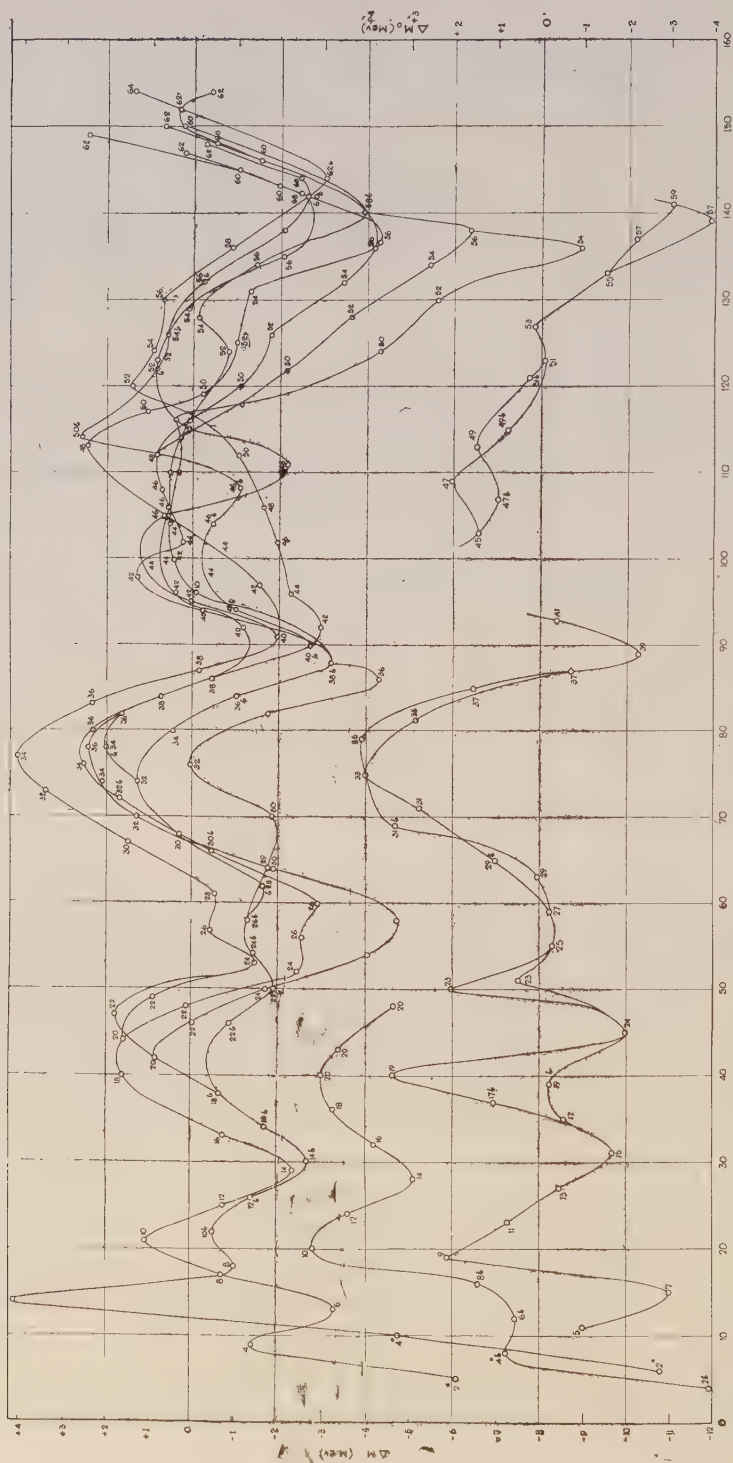


Fig. 1- ΔM -A curves for even and odd charge stable nuclei with scales on the left and right sides respectively. Few unstable nuclei are marked with asterisk. The charges are indicated at the points. Most strongly bound nuclei are denoted by 'b' in addition.

with the values of the four constants as given by Green (1954). The experimental data have been taken from the work of Duckworth (1958) up to atomic number $Z = 62$ for which range the nuclear masses of all the stable isotopes are given except for $Z = 44$. For the selection of the points through which to draw a certain curve, we have divided the nuclei into two sets, one with odd values of Z and the other with even values of Z . The set of even values of Z is further subdivided into categories depending upon the excess number of neutrons over protons, whether it is none, one, two, three and etc. When the minimum excess of neutrons changes from one stable element to the next one, the curve is drawn connecting the two minimum excess isotopes even though the excess of neutrons is not the same along the curve. Further when the total number of stable isotopes varies from one element to the next, there is branching or merging of curves depending upon whether the number of isotopes increases or decreases at that point: in the case of ambiguity mostly, near the region of branching or merging the points are so chosen that the curve connecting them follows a regular smooth course.

The curves drawn in accordance with the principles stated above show regular undulating character with a smooth run, the maxima and minima of all the different courses fall at near about the same region of mass number.

From the above curves it is possible by way of interpolation to predict the values of masses of the isotopes of $Z = 44$ which are not tabulated by Duckworth. The element $Z = 44$ has seven stable isotopes with mass number $A = 96, 98, 99, 100, 101, 102$ and 104 : Duckworth has given the masses of the isotopes with $A = 96, 102$ and 104 . By the method of interpolation of curves we have calculated the possible masses of the remaining isotopes. After the completion of this work it has come to our notice that Everling (1960) has supplied the masses of $A = 98$ and 99 as well as of $A = 96, 102$ and 104 , and the agreement of our extrapolated results with Everling's for $A = 98$ and 99 is as good as that of Everling's results with Duckworth's for $96, 102$ and 104 .

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ON THE APPLICABILITY OF DEBYE'S THEORY IN THE DETERMINATION OF THE TIME OF RELAXATION IN THE CASE OF PURE LIQUIDS

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It is well known that in the case of polar liquids the dipole moment of polar molecules cannot be determined from the polarization of the pure liquid by applying Debye's expression. The object of the present note is to point out that there is some justification in applying Debye's equation for the polarization at high-frequency oscillating field for the determination of the value of τ , the time of relaxation even in the case of pure liquids.

In the case of dilute solutions Whiffen and Thompson (1946) have taken the condition for maximum absorption as that for the maximum value of ϵ'' and the latter occurs when,

$$\omega_{max} \tau_0 = 1 \quad \dots (1)$$

This is justified in the case of dilute solution, because ϵ' may be assumed to be independent of frequency, ϵ' and ϵ'' being the real and imaginary parts respectively of the complex dielectric constant ϵ^* . It is to be noted, however, that this condition for maximum absorption deduced by previous workers for solution is the condition for the occurrence of maximum value of ϵ'' and not of $\tan\delta$, and therefore, it is not applicable to pure liquids. If we want to find out the condition for maximum value of $\tan\delta$ in the case of pure liquids we find that $\tan\delta$ will be maximum when,

$$\omega \tau_0 = \sqrt{\frac{\epsilon_1}{\epsilon_0}} \quad \dots (2)$$

where ϵ_1 is the dielectric constant for static field and ϵ_0 that for a field of infinite frequency.

Hence, the condition $\omega_{max} \tau_0 = 1$ cannot be applied in cases of pure liquids, because in such cases ϵ_1/ϵ_0 is much greater than unity and according to Eq. (2) $\omega \tau_0$ is greater than unity.

On the other hand, according to Debye's equation, the condition for maximum absorption is given by

$$\omega_{max} \tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \cdot \sqrt{\frac{\epsilon_1}{\epsilon_0}} \quad \dots (3)$$

Taking a typical case of benzyl chloride for which $\epsilon_0 \approx n^2 = 2.4$ and ϵ_1 is about 8, we get from Eq. (3), $\tau = 0.792/\omega_{max}$, but from Eq. (1) we get $\tau_0 = \frac{1}{\omega_{max}}$

$$\therefore \frac{\tau}{\tau_0} = 0.792$$

So, the value of τ deduced from Debye's equation is about 20% smaller than that deduced from Eq. (1). Since the radius of the rotor is proportional to $\tau^{1/3}$ this difference will not affect the radius of the rotor by more than 7%. This explains why in the case of liquids with molecules having the OH group as a substituent the radius of the rotor deduced from Debye's equation (Ghosh, 1945a, b, 1955a, b, c) was found to be appropriate for the OH group.

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COHESIVE ENERGIES AND OTHER PROPERTIES OF IONIC CRYSTALS

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Many properties of gases and liquids have been calculated and explained in terms of a commonly used interaction energy function, such as Lennard-Jones (12:6) potential. In an ionic crystal, the charge distribution on each ion has approximately spherical symmetry and they interact according to central force law. Thus, it seems reasonable to assume that ions of an ionic crystal are of the same electronic structure as an inert gas, possess overlap energy (and Van der Waals energy), following a law with the same interionic distance variation as for two inert gas atoms. It is therefore, possible to describe a number of properties of ionic crystals on a common basis with the help of Lennard-Jones (12:6) potential in conjunction with the term for Coulomb energy. This, thus, affords a unified approach for evaluating and interpreting the properties of ionic crystals as well as the knowledge about the interaction forces and it is reasonable to assume that such an analysis will achieve considerable success.

The energy per cell in an ionic crystal may be represented as

$$\phi(r) = \left(-\frac{\alpha e^2}{r} + \frac{B}{r^{12}} - \frac{C}{r^6} + \epsilon_0 \right) \quad \dots \quad (1)$$

where α is Madelung's constant, e is the electronic charge, r is the interionic distance, B is the repulsive parameter which is calculable, C is the Van der Waals constant and ϵ_0 is zero point vibrational energy.

In Eq. (1) we have not considered the dipole-quadrupole Van der Waals term and effect of overlap potentials other than the nearest neighbours because they do not alter the estimates of various properties appreciably.

Finding the first and second derivatives of Eq. (1) and equating it with the well known expressions involving compressibility, molar volume and temperature (Huggins, 1937) expressions for the parameters B and C can be derived and their values obtained with the help of the experimental data for various observable properties. Alternatively, B can be obtained in the above manner and C can be used directly from the optical data of Huggins and Mayer (1933).

TABLE I

Crystal	Cohesive energy in <i>K</i> Cal/mole				Compressibility in 10 ⁻¹² cm ² /dyne			Coefficient of thermal expansion × 10 ⁶		
	Experi- mental	Calcu- lated (present work)	Calcu- lated (Fowler)	Calcu- lated (Cubiccio- tti) ^a	Calcu- lated (Huggins)	Experimental ^a	Calcu- lated (present work)	Experi- mental	Calcu- lated (present work)	Calcu- lated (Born model) ^b
CsF	—	182.4	176.9	179.2	175.7	4.25	(4.25)	—	—	—
CsCl	157.8	156.8	157.3	155.9	153.1	5.95	(5.55)	56.0	55.27	56.18
CsBr	152.3	151.6	153.5	151.1	149.6	7.06	(6.28)	—	—	—
CsI	145.4	142.9	147.7	143.6	142.5	8.57	(7.83)	—	—	—
	(141.5) ^H									
RbCl	163.6	167.0	165.7	164.3	162.0	6.65	(6.16)	36.0	31.52	41.05
RbBr	158.0	162.6	160.6	157.6	156.1	7.94	(7.38)	38.0	42.61	41.90
RbI	149.7	150.1	153.5	149.1	148.0	9.57	(9.00)	—	—	—
KBr	161.2	165.5	166.3	162.7	161.3	6.70	(6.45)	40.0	37.44	43.08
KI	152.8	155.1	158.8	153.4	152.4	8.54	(8.07)	—	—	—
NaI	166.3	166.8	170.8	165.9	164.3	7.07	(6.21)	48.3	47.99	42.87

(H) Huggins (1937)

(a) Cubicciotti (1959)

(b) Kumar (1960)

pressions can be derived for various crystal properties and the values of the B and C can be used to compute them. Following this scheme we calculated the values of the cohesive energy, compressibility and the coefficient of linear expansion for a few representative alkali halide crystals (reported in Table 1,) and compared them with the experimental values and also with other determinations. The results based on the Lennard-Jones (12:6) potential are quite consistent with other determinations. The discrepancies with the experimental data become more pronounced as we proceed towards lighter alkali halides but the agreement is quite satisfactory for heavier compounds. Details and also computations for other metal halide crystals heavier than alkali halides will be published later.

ACKNOWLEDGMENT

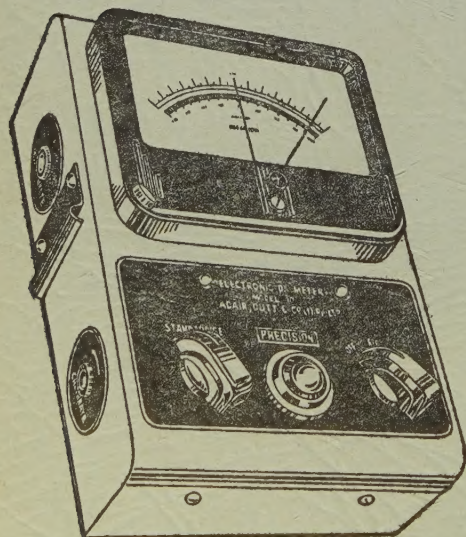
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